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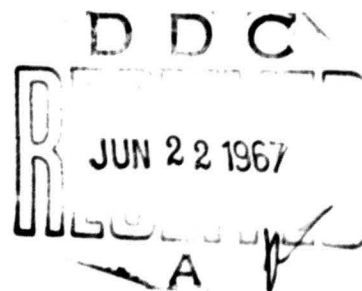# ADHESIVE BONDING OF STAINLESS STEELS

By R. E. Keith, M. D. Randall, and D. C. Martin

Prepared Under the Supervision of the
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Directorate of Research and Development
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ADHESIVE BONDING OF STAINLESS STEELS

By

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ABSTRACT

This report covers the state of the art of adhesive bonding of stainless steels. Typical joint designs, surface preparation procedures, and environmental factors are described as they influence choice among the available adhesives and processing techniques. Both organic and inorganic adhesives are covered.

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PREFACE

This report is one of a series of state-of-the-art reports being prepared by Battelle Memorial Institute, Columbus, Ohio, under Contract DA-01-021-AMC-11651(Z), in the general field of materials fabrication.

This report deals with the adhesive bonding of stainless steels, and is oriented toward the interests of the designer and the manufacturing engineer. The processing incident to adhesive bonding, the types of ahdesives used for bonding stainless steels and the available test results on adhesive-bonded stainless steels are included in the report.

In accumulating the information necessary to prepare this report, the following sources within Battelle were searched for the period from 1957 to the present:

> Main Library
> Slavic Library
> Chemistry Library
> Defense Metals Information Center
> Atomic Energy Commission Library

Outside Battelle, the following information centers were searched:

> Redstone Scientific Information Center
> Defense Documentation Center
> Plastics Technical Evaluation Center
> NASA

In addition to the literature search, personal contacts were made by telephone or visits with the following organizations and individuals:

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Bell Helicopter Company
Fort Worth, Texas

Floyd H. Bafr
Materials Laboratory
Wright Patterson Air Force Base
Ohio

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Lockheed California Company
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SUMMARY

Stainless steels can be successfully adhesive bonded using presently available techniques and adhesives. Service temperatures for stainless steels, however, are often above the present maximum service temperatures or organic adhesives. Inorganic adhesives of sufficient mechanical shock resistance have not been developed to compete effectively with brazing anu welding for joining high-temperature structures. Also, bond-line thicknesses of inorganic adhesive-bonded joints are considerably thicker than those of brazed joints resulting in incre sed weight. As the maximum service temperatures of new organic adhesives continue to increase, production applications of adhesive bonding to stainless steels should become increasingly attractive. Since the principles of adhesive bonding are generally similar for all metals, the information contained in this report is expected to be useful for such anticipated applications, as well as for the occasional specialized applications that may be presently encountered.

The preparation of the metal surfaces prior to bonding has a marked effect on the strength and quality of the joints obtained. Particular attention must be given to metal-surface preparation for joints intended to be used at elevated temperatures or at cryogenic temperatures.

For successful production of quantities of adhesive-bonded assemblies having uniformly high mechanical properties, careful inspection and quality-control procedures are essential throughout the manufacturing process.

Continual monitoring of adhesive characteristics, compositions of surface-preparation solutions, adjustment of processing equipment, accuracy of process control instruments, and testing of completed joints is essential.

INTRODUCTION

Adhesive bonding, the various forms of welding, brazing, and soldering, and mechanical fastening, comprise the available methods for joining of materials. All five of these methods have long been in use because each joining method has particular advantages that are responsible for its continued use. Each method has its drawbacks. For example, welding can result in the lightest joints; mechanical fastening usually results in the heaviest joints. On the other hand, welded joints are permanent, whereas mechanically fastened joints can be made to be taken apart. Welded joints are usually made at high temperatures, at or near the melting point of the metal. Adhesive bonding may require no external heating at all. The range of dissimilar metals that can be joined by welding is severely limited by metallurgical and physical property considerations. Adhesive bonding can be used with relative freedom not only to join dissimilar metals, even in thin sections, but to join metals to wood, ceramics, and plastics as well.

Many other comparisons could be made among the different joining processes, but those given above are illustrative of the considerations that result in one method being chosen over the others to make a joint for a given application. This report deals specifically with adhesive bonding as applied to stainless steels.

The steps necessary to make an adhesive bond are shown in Figure 1. The surfaces to be joined, usually referred to as the adherends, must be properly

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For Inorganic Adhesives:

Pretreatment

Clean Adherends

Condition Adherend
Surfaces

Prime

Apply Adhesive

Position Adherends
Securely

Making the Joint

Cure

Posttreatment

Postcure

Clean

Inspect

Finish

Smelt Adhesive

Frit

Blend With Additives

Prepare Slip
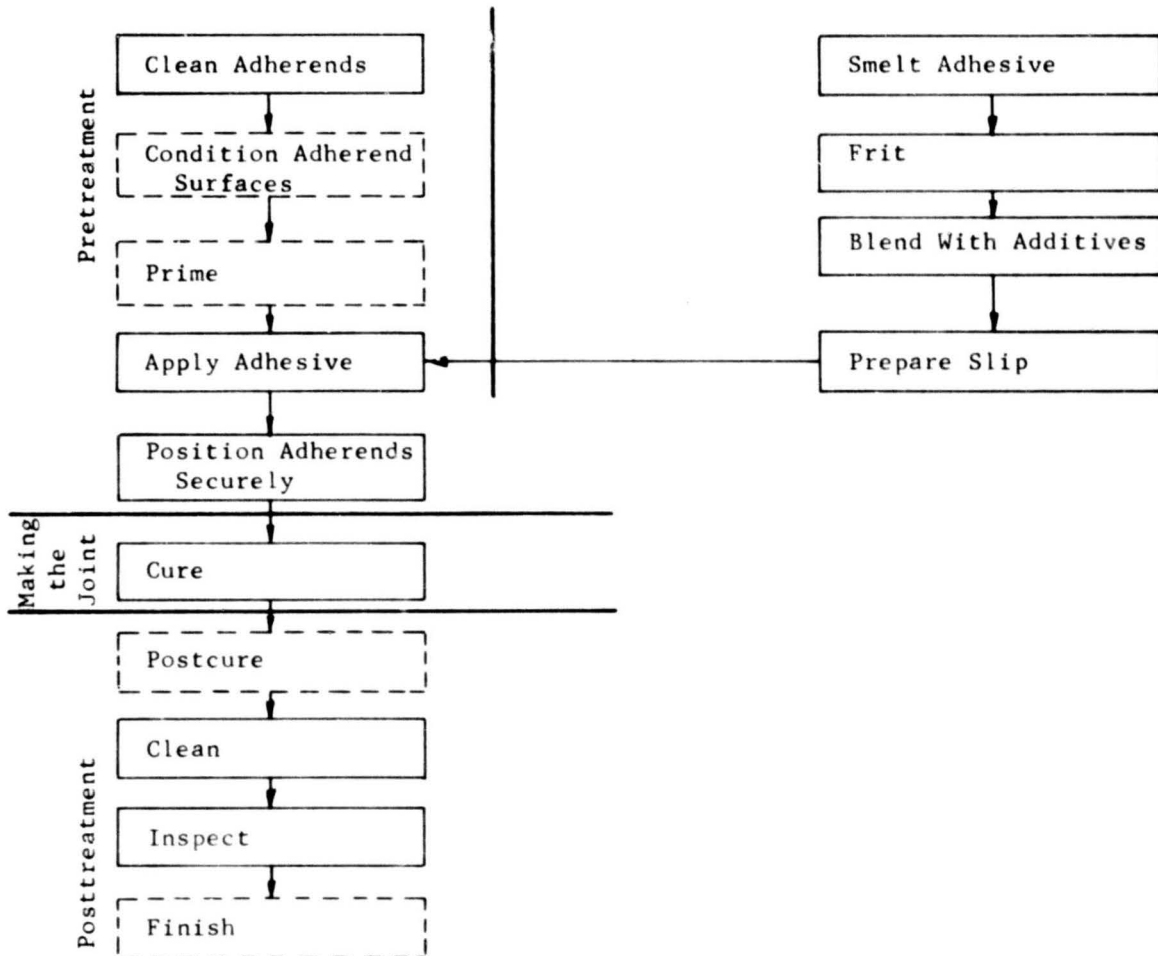
FIGURE 1. SCHEMATIC DIAGRAM OF OPERATIONS PERFORMED IN
ADHESIVE BONDING

Dashed boxes indicate steps not always performed.

cleaned and conditioned. The conditioning may involve application of an electrolytic or a chemical-conversion coating, and may be followed by application of a primer adhesive in a volatile solvent. The substance used to form the bond, known as the adhesive, is placed on the area to be bonded. The adherends are placed in the desired relative position, both adherends being in contact with the adhesive, and some means of maintaining them in this relationship is provided. Time is allowed for the adhesive to cure, or harden; during this period many adhesives require the application of external heating. After the cure, the adhesive, now a solid, is hopefully uniformly distributed as a film several thousandths of an inch thick between the adherend surfaces. When viewed in cross section, the plane of adhesive has the appearance of a thin line, referred to as the glue line, or bond line. The joint is now complete, although for some applications a second during cycle, or postcure, is desirable. Posttreatment of the joint may include removal of any excess adhesive that has oozed out of the bond area. For critical adhesive joints, nondestructive testing is employed, following which the joint may be painted.

When inorganic adhesives are used, the bonding procedure differs somewhat. Since inorganic metal-bonding adhesives are not generally available commercially, it is necessary to prepare the adhesives from raw materials. These are typically inorganic chemicals similar to those used in glass manufacture. The proper mixture of raw materials is fused or smelted at a temperature that may be as high as 4500 F depending on composition. The melt is then poured into water. This quenching operation, referred to as fritting, rapidly cools the adhesive and results in the formation of a coarse powder or frit. The frit may be blended with additives prior to use. These additives may be metal or metal-oxide powders, which are added to improve the bond strength, or they may be materials added to stabilize the water suspension, or slip, the form in which

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the adhesive is to be ultimately applied. After the additives have been mixed

with the frit, they are blended in a milling operation, during which the

particle sizes are reduced. When the desired range and distribution of

particle sizes has been attained, as evidenced by screening analysis, water

is mixed with the powder to form the slip. The slip is then ready for applica-

tion to the adherends. The remaining steps in the bonding process with inorganic

adhesives are similar to those using organic adhesives, except that the curing

step is referred to as maturing. Maturing temperatures are typically much higher

than curing temperatures of organic adhesives.

The increasing interest in adhesive bonding as a practical means of joining

of metals is attested to by the large number of books and handbooks (Refs. 1-7),

bibliographies (Refs. 8-12), symposia transactions (Refs. 13-21), and summary

articles (Refs. 22-31), which have appeared during the last several years. The

reader is referred to these publications for a general background in metal-to-

metal adhesive bonding. The bulk of the metal-adhesive-bonding work done in

this country has been on aluminum, and the largest volume of literature is

concerned with bonding of various aluminum alloys. Stainless steels have

also been adhesively bonded with organic adhesives. The majority of the

development work on inorganic (ceramic) adhesives has been done using

precipitation-hardening stainless steel adherends.

STAINLESS STEELS

Several different groups of alloys are included in the general category

of "stainless" steels. Composition limts of the more commonly used stainless

steels are given in Table I. The term "stainless" itself is a misnomer, since

some chemical agents will attack these materials. It may be because of

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TABLE I. COMPOSITIONS OF SOME WIDELY USED AUSTENITIC STAINLESS STEELS (Ref.32)

Alloy	C, max	Mn	Si,max	Cr	Ni	Other
				Composition, percent		
201	0.15	5.50-7.50	1.00	16.00-18.00	3.50-5.50	0.25 max N
202	0.15	7.50-10.00	1.00	17.00-19.00	4.00-6.00	0.25 max N
301	0.15	2.00 max	1.00	16.00-18.00	6.00-8.00	
302	0.15	2.00 max	1.00	17.00-19.00	8.00-10.00	
303	0.15	2.00 max	1.00	17.00-19.00	8.00-10.00	0.16 min S
304	0.08	2.00 max	1.00	18.00-20.00	8.00-12.00	
310	0.25	2.00 max	1.50	24.00-26.00	19.00-22.00	
316	0.08	2.00 max	1.00	16.00-18.00	10.00-14.00	2.00-3.00 Mo
321	0.08	2.00 max	1.00	17.00-19.00	9.00-12.00	5XC min Ti
347	0.08	2.00 max	1.00	17.00-19.00	9.00-13.00	10XC min Cb-Ta

objections to calling these steels stainless that they are sometimes designated in the aerospace industry by the American Iron and Steel Institute (AISI) type number followed by the letters CRES. CRES is an acronym for "Corrosion-REsistant Steel". In this report the more familiar designation, stainless steel, will be used.

There are three series of wrought alloys known as "conventional" stainless steels, designated by the AISI as Series 200, 300, and 400. The 400 series alloys are not austenitic and are bonded using procedures similar to those for carbon steels and low-alloy steels. This report is concerned with the adhesive bonding of those stainless steels that consist principally or entirely of austenite, the face-centered cubic crystal structure of iron.

Series 200 Stainless Steels. These are alloys designed during and after the Second World War as substitutes for the 300 series alloys. They contain smaller quantities of nickel than the 300 series alloys, manganese and nitrogen being substituted. The 200 series alloys are not heat treatable.

Series 300 Stainless Steels. The 300 series alloys are the oldest and most common stainless steels. Their compositions are variations from the basic Fe-18Cr-8Ni composition. As a class, they are austenitic, nonmagnetic alloys, although some may be ferromagnetic under some conditions. Properties of these alloys cannot be improved by heat treatment.

Precipitation-Hardening Stainless Steels. In recent years, alloys have been introduced that contain small amounts of such elements as titanium and aluminum. These elements render the alloys heat treatable.

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The precipitation-hardening stainless steels are grouped into three types:

(1) Martensitic

(2) Semiaustenitic

(3) Austenitic.

This classification is based on the behavior of the steel when it is cooled from an appropriate austenitizing (solution treating) temperature.

In martensitic types, the austenite transforms to martensite on cooling. This transformation causes some hardening. Additional strength is obtained by aging at the proper temperature.

After cooling from the austenitizing temperature to room temperature, the semiaustenitic types remain austenitic. Reheating to an appropriate temperature conditions the austenite so that it transforms to martensite on cooling to room temperature or lower. Subsequent aging at the proper temperature increases strength over that obtained by the austenite-martensite transformation.

The austenitic types do not transform on cooling to room temperature. Strengthening is obtained by aging the austenitic structure at an appropriate temperature. Table II shows the compositions of a number of precipitation-hardening stainless steels.

For a complete discussion of the stainless steels, the reader is referred to a standard work on the subject, such as the ASM Metals Handbook (Ref. 32).

The curing temperatures required for adhesive bonding with organic adhesives are below the heat treatment temperatures, if any, for the stainless steels. If heat treatments of the adherends are required, they are performed prior to organic adhesive bonding. The maturing cycle for ceramic adhesives may be combined with the final heat treatment for precipitation-hardening stainless

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TABLE II. COMPOSITIONS OF COMMERCIAL PRECIPITATION-HARDENING STAINLESS STEELS (Ref. 33-37)

Alloy	C	Mn	Si	Cr	Ni	Al	Mo	Other Elements
							Composition, percent	
Austenitic Types								
A-286	0.08 max	1.0-2.0	0.40-1.00	13.5-16.0	24.0-28.0	0.35 max	--	1.0-1.5Ti, 0.10-0.50V
17-10P	0.10-0.14	0.50-1.00	0.60 max	16.5-17.5	9.75-10.75	--	--	0.25-0.30P
HNM	0.30	3.50	0.50	18.50	9.50	--	--	0.25P
Martensitic Types								
Stainless W	0.12 max	1.0 max	1.0 max	16.0-18.0	6.0-8.0	1.0 max	--	1.0Ti max, 0.2N max, 1.0Al max
17-4 PH	0.07 max	1.0 max	1.0 max	15.5-17.5	3.0-5.0	--	--	3.0-5.0Cu, 0.15-0.45Cb+Ta
15-5 PH	0.07 max	1.0 max	1.0 max	14.0-15.5	3.5-5.5	--	--	2.5-5.5Cu, 0.15-0.45Cb+Ta
414 Ti	0.08 max	1.0 max	0.75 max	10.5-12.5	1.5-3.5	--	--	0.75Ti max
ALMAR 362 (typical)	0.03	0.3	0.20	14.5	6.5	--	--	0.80Ti
ALMAR 363	0.05 max	0.3 max	0.15 max	11.0-12.0	4.0-5.0	--	--	10XC min Ti
Semiaustenitic Types								
17-7 PH	0.09 max	1.0 max	1.0 max	16.0-18.0	6.5-7.75	0.75-1.50	--	--
PH 15-7 Mo	0.09 max	1.0 max	1.0 max	14.0-16.0	6.5-7.75	0.75-1.50	2.0-3.0	--
AM-350	0.12 max	0.90	0.50 max	16.0-17.0	4.0-5.0	--	2.5-3.25	0.10N
AM-355	0.15 max	0.95	0.50 max	15.0-16.0	4.0-5.0	--	2.5-3.25	0.10N

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steels, but for organic adhesive bonding of the precipitation-hardening stainless steels, procedures are similar to those for the conventional stainless steels, and it is appropriate to include both types of stainless steels in the same report.

ADVANTAGES OF ADHESIVE BONDING

It is appropriate to review briefly the advantages and disadvantages of the adhesive bonding process itself. Knowledge concerning adhesive bonding is not yet as widespread throughout industry as is knowledge of such other joining techniques as riveting, welding, and brazing.

Advantages of adhesive bonding include:

(1) Mechanical strength

(2) Mechanical damping

(3) Smooth external appearance

(4) Electrical insulation under some conditions

(5) Capable of joining dissimilar materials

(6) Usable with thin or brittle materials

(7) Possible weight and size reduction

(8) Combined sealing and structural function

(9) Minimum finishing required

(10) No thermal damage to metals

(11) May be least expensive joining method.

Adhesive-bonded joints ade with organic adhesives, when properly designed and fabricated, have lap-shear tensile strengths at room temperature up to 7000 psi, and in some cases fracture includes pieces of metal pulled from the surface at the bond plane. Not only do the tensile strengths of adhesive-bonded joints

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compare favorably with riveted and spot-welded joints, but adhesive-bonded joints are often superior under cyclic-loading conditions. They distribute the load more uniformly across the joint than is possible with rivets or spot welds.

The high damping capacity of organic adhesives relative to metals is advantageous in reducing sensitivity of a structure to vibrational loading and contributes to the lowering of noise level.

Smooth, unbroken lines are obtainable by adhesive bonding. A smooth exterior surface is an absolute requirement for such applications as high-speed aircraft. There are many other applications where smooth contours contribute to the pleasing appearance of a product.

Since organic adhesives are electrical insulators, they may serve to isolate structural members that are joined by adhesive bonding. In cases were electrical isolation is not desired, a limited electrical conductivity can be provided in the adhesive, or direct metallic connection can be made between the adherends. If the primary purpose of a joint is for electrical insulation, however, superior insulators are available, and the joint must be designed to provide sufficient insulator path length to avoid electrical leakage.

The electrical insulating properties of adhesives make possible the joining of dissimilar metals with much reduced danger from galvanic corrosion. This characteristic gives a designer increased freedom in materials selection.

The often-cited claim that adhesive-bonded joints can be expected to provide electrical insulation between adherends has recently been questioned by Heimel (Ref. 38). Resistance measurements of a large number of production joints were made and it was found that in every joint there was electrical continuity.

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Keimel attributed this to local asperity contact between the adherends through the adhesive. It is to be noted, however, that an unsupported fluid adhesive was used. Adherend insulation, if it had been desired, might have been achieved using a supported film or tape adhesive.

Adhesive-bonded joints can be made easily with very thin materials, such as paper and metal foil. Both mechanical fastening and welding become difficult for thin material. Freedom from high intensity or sudden mechanical loading during the making of an adhesive-bonded joint is also an advantage when joining brittle materials.

Butt-welded joints are the lightest possible type of construction. Adhesive-bonded-lap joints, although they are inherently heavier than butt joints, nevertheless may offer considerable weight and size advantage over mechanically fastened lap joints in cases where parts are small, thin, or light. or would otherwise have to be joined with large numbers of fasteners.

Certain adhesives, notably the elastomers and elastomer-phenolic blends, are frequently used as sealants as well as structural adhesives. One example of their use for this purpose is in the so-called "wet wing" type of aircraft construction, in which no separate fuel tank is used. The fuel in this instance is contained within the wing by 100 percent sealing of structural joints.

Following curing of the organic-adhesive-bonded joint, there is little or no further work necessary. It may be desirable to remove any small amount of adhesive that extends beyond the joint, but this is easily accomplished. Most joints are put in service without further attention after curing. Oxidation which occurred on adherend surfaces during maturing of inorganic adhesives may have to be removed.

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The curing temperatures required for most organic adhesives are below the temperature range that will cause alternation of the metallurgical structure of the common metals. In an adhesive-bonded joint there is nothing corresponding to the heat-affected zone of a weld. However, in the case of inorganic adhesives and some organic adhesives for high-temperature service, curing temperatures may be high enough to cause alteration of the metallurgical structure of the adherends.

When the entire cost of making a joint is accounted for, adhesive bonding may be found to be less expensive than other methods of joining. Such factors as capital costs associated with tooling and fixturing, special joint preparation, bond-area coverage per unit volume of adhesive, finishing, and the associated labor costs must be considered. These costs must be balanced against all corresponding costs for other joining methods.

DISADVANTAGES OF ADHESIVE BONDING

As with any process, there are certain limitations and drawbacks to adhesive bonding. These include:

(1) Limited service conditions

(2) Residual stresses

(3) Accurate joint fitup required

(4) High standard of cleanliness

(5) Subject to weathering, solvent, and moisture attack

(6) Curing time required to develop maximum properties

(7) Adhesive may react with the material being joined

(8) Adhesive may outgas

(9) Adhesive may degrade under radiation.

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The upper-service-temperature limit that a good expoxy or phenolic adhesive can withstand for an indefinite time is usually given as about 350 F. Although adhesives are available that will withstand short-time exposure at 900 F and about 1000 hours at 500 F (Ref. 39), and some Russian work reports tests made at temperatures up to 1832 F (Ref. 40), allowable service time at high temperatures for adhesive-bonded joints is limited.

The presence of residual stresses in an adhesive-bonded joint becomes an increasingly serious problem as curing temperature increases. The stresses arise partly because of differential thermal expansion between the adhesive and the adherend. Typically the thermal-expansion coefficient of the adhesive is greater than that of the metal adherend, so the adhesive layer is put in tension as the joint cools following curing. Unlike the residual stresses resulting from welding, these residual stresses cannot readily be annealed out. They can be minimized, however, by using a thicker glue line, by altering the adhesive composition to make it more resilient, and by postcuring.

Clearance between adherends to be adhesively joined should be uniform and usually somewhere between 0.005 and 0.010 inch. This is a more accurate fitup tolerance than some plants are accustomed to using.

Any but the most rudimentary joining process requires at least some treatment of the surface prior to making the joint, even if it is only removal of the burr around a drilled hole. In welding, this surface is obtained by melting away the surface layers of metal. In brazing and soldering, surface films are removed by fluxing. In adhesive bonding, where neither of these methods can be used as presently practiced, adherend surfaces must be pretreated and kept clean until bonded. The difficulty of accomplishing the

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necessary surface treatment depends upon the accustomed standards within a particular plant or industry, and often it represents no major changes from practices already in use for preparing a surface to be painted.

Care must be exercised in the choice of an adhesive for a given application, since there is danger of degradation of the adhesive by its environment. Thermoplastic adhesives, in particular, are subject to attach by solvents. Cyanoacrylates are moisture-sensitive. Intelligent choice among the many available adhesives can minimize the dangers from the service environment.

In some manufacturing operations, the curing time for an adhesive-bonded joint presents a problem. Typically, this time ranges from a few minutes to several hours. During this period, the adherends must be fixtured so that there is no relative motion between them. There are possibilities of reducing the magnitude of this disadvantage. In some cases the parts can be designed so as to be self-registering, for example. In some applications, the adhesive cure is accomplished at the same time the paint is baked on.

Care must be taken in the selection of adhesives, fillers, extenders, and curing agents to avoid compounds that will corrode the adherends. For example, amine-cured adhesives are corrosive to copper-base alloys. The magnitude of the problem can be appreciated when it is realized that there are over 100 different curing agents for epoxy resins on the market today, many under trade names that give no indication of their composition. There is no substitute for knowledge and testing experience at this point.

Use of any organic material in enclosed or hermetically sealed devices should be with caution, since sufficient vapor may be given off from the organic material during and after curing to impair the function of the device.

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Considerable difficulty has been encountered in the past with contact fidelity in small electrical relays from deposits traceable to volatile components and decomposition products from organic materials.

While all materials are damaged by radiation, rates of accumulation of damage to the relatively delicate molecules of organic materials are greater than for metals exposed to the same radiation. Adhesive bonding with organic adhesives is the most radiation sensitive of the joining processes. Ceramic adhesives, on the other hand, are among the least sensitive materials to radiation.

With the present state of the art, inorganic adhesives do not possess the advantages previously cited to the same extent that organic adhesives do. The high mechanical strengths obtained using inorganic adhesives, in the 9000-psi range, are considerably higher than the highest strengths that have been obtained with organic adhesives. Inorganic adhesives tend to be brittle, however, and possess little damping capability. Inorganic adhesives intended for metal bonding may contain metal powders that may provide electrically conductive paths. The higher density of inorganic adhesives and the necessity to maintain bond-line thicknesses of the order of approximately 0.010 inch to assure uniform joint filling are unfavorable for weight reduction. High maturing temperatures required with inorganic adhesives may cause metallurgical damage to the adherends, although it is sometimes possible to combine the adhesive maturing treatment with the adherend heat treatment. Not enough inorganic-adhesive bonding has been done to make an accurate estimate of its economics relative to other joining methods.

On the other hand, inorganic adhesives in comparison with organic adhesives are: (1) usable at higher temperatures, (2) require less elaborate adherend preparation, (3) not as sensitive to weathering, solvent,

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and moisture attack, (4) outgas less in service, and (5) more radiation-resistant.

To summarize, adhesive bonding is a joining process that has unique advantages. It supplements other joining techniques, and, when full advantage is taken of the design opportunities offered by adhesive bonding, it may supplant the more traditional metal-joining processes in a surprising number of applications. However, failure to allow for the limitations and peculiar characteristics of adhesives can lead to unsatisfactory results.

GENERAL COMMENTS ON ADHESIVE BONDING
OF METALS

It is beyond the scope of this report to go into detail concerning adhesion theory. The reader is referred to the general references cited earlier for information on the subject. In this section, some principles which are particularly important in metal-to-metal adhesive bonding will be mentioned briefly.

ADHESION MECHANISMS

Any adhesive, to be effective, must wet the adherend surface. Although the forces of adhesion of organic materials to metal surfaces are not clearly understood, it is known that these are short-range forces with respect to the molecular dimensions. Therefore, presence of foreign substances that do not permit the close approach of the adhesive molecules to the metal surface is likely to result in poor bonding.

In the case of inorganic adhesives, the bonding mechanism appears to involve transport of adherend ions into the adhesive as well as transport of metal ions from the adhesive into the surface layer on the adherend. Adherends to be bonded with inorganic adhesives are often deliberately oxidized, then

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pickled, prior to bonding. This heat-scaling operation by removal of the oxide formed, possibly serves to set up beneficial alloy concentration gradients at the adherend surface that improve wetting or shorten the diffusion time necessary to establish a strong bond across the metal-oxide interface. Specifically, the adherend surface would have been depleted in chromium, silicon, and manganese, and enriched in nickel.

A significant finding of the programs on inorganic adhesives development was that presence of a glassy phase was necessary for the formation of a strong adhesive joint. Crystalline ceramics, air-drying cements, and recrystallizable glasses were all examined, but gave inferior results.

DIFFERENTIAL DIMENSIONAL CHANGES

Thermal expansion coefficients of adhesives as a class of materials are higher than those of metals. As has been mentioned previously, the mismatch in thermal expansion coefficients can cause residual stresses in the joint with temperature changes. An adhesive bond will tend to be under internal stress on cooling after the cure, the adhesive tending to be in tension. If there has been shrinkage of the adhesive during the cure, the tensile stress in the adhesive will be further increased in the completed joint. Delayed room-temperature failure of joints due to these residual stresses is a fairly frequent occurrence during the developmental stage of an adhesive-bonding application, particularly when the bond area is large. This problem can usually be solved by adjustment of the curing cycle. If the joint is intended for service below room temperature, even greater stresses will develop during cooling to the service temperature, which may result in immediate and spontaneous failure of the bond.

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One method sometimes used to reduce thermal expansion mismatch is to fill the adhesive with metal powder, preferably of the metal being bonded. This is done with risk of causing loss of adhesion, however.

Adhesives intended for use with metals are often complex mixtures of an epoxy or phenolic resin blended with an elastomer, such as nitrile rubber, or a thermoplastic, such as nylon. The purpose of these latter materials is to increase the resiliency of the adhesive. A resilient adhesive is better able to accommodate to the internal stresses in the joint and to resist failure by peeling than a hard or brittle one (Figure 2).

USE OF SOLVENT CARRIERS

Adhesives intended for use in the bonding of metals, ceramics, and glasses usually contain only small amounts of the solvents or other volatile materials that are commonly found in adhesives intended for use with such porous materials as wood, concrete, paper, and leather. The inability of solvents, if used, to escape from between nonporous surfaces leads to greatly extended cure times and may result in porous bonds. Primers for metal joints do contain solvents, but it is intended that these solvents be allowed to evaporate before the bonding operation is carried out. Adhesives containing solvents can be used with metals if they are coated and left apart until most of the solvent has evaporated, but the most widely used metal adhesives, such as the epoxies and phenolics, contain little or no solvent. Phenolics do liberate water on curing, however, and joints bonded with them should be vented and securely clamped.

Inorganic adhesives, regardless of the method of application, will generally contain some water. Heating rates must be controlled to allow this water to escape slowly. Adherends must be rigidly fixed to prevent any movement during water evolution.

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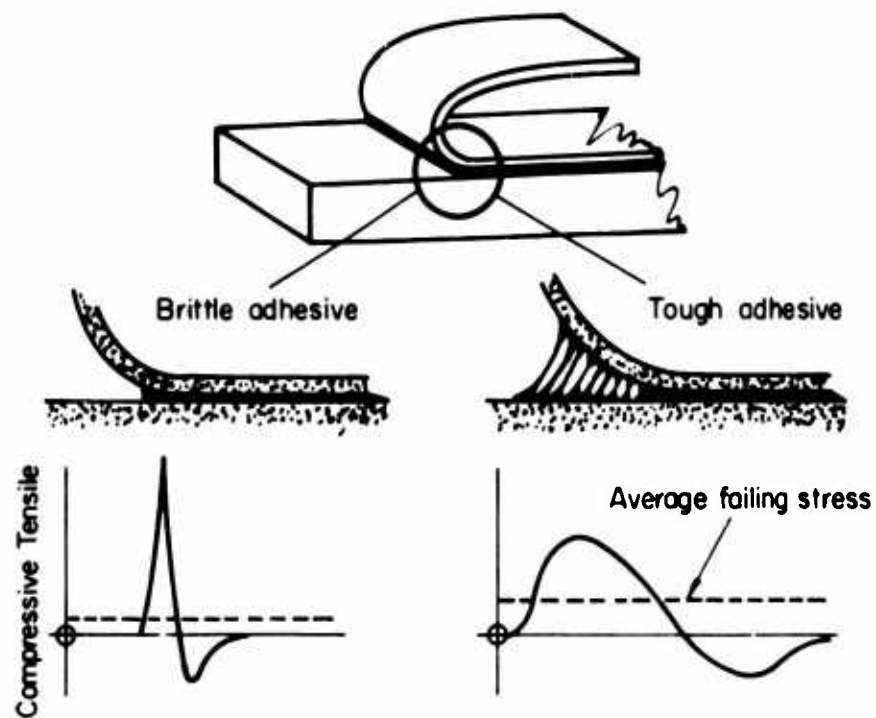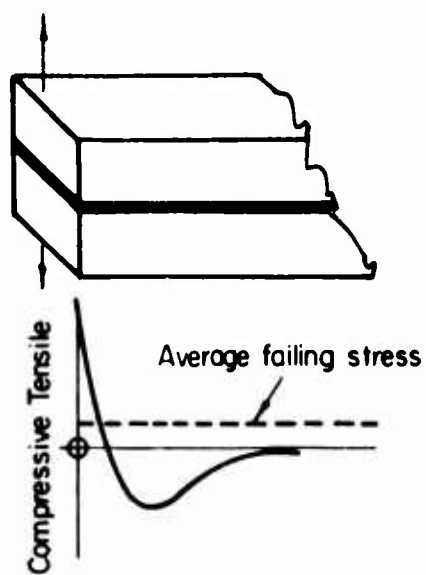
a. Peel Stresses

b. Cleavage Stresses

A-54361

FIGURE 2. PEEL AND CLEAVAGE STRESSES IN ADHESIVE-BONDED JOINTS (REF. 31)

BONDING STAINLESS STEELS WITH ORGANIC ADHESIVES

DESIGNING THE JOINT

Since the best strength properties of adhesives are typically those obtained under shear loading, lap joints are the preferred type where possible. The detailed stress analysis of an adhesive-bonded joint is difficult, partly because of the nonlinear stress-strain characteristics of adhesives. Stress analyses have been made, however, and a recent survey report (Ref. 41) presents a critical review of the present knowledge in this area. For purposes of this report, it is sufficient to point out that stresses are not uniformly distributed across an adhesive joint. Stress concentrations occur at the free edges of the glue line, as shown in Figure 3. If the adherends are thin enough to bend as shown in Figure 3, the stress concentrations in the plane of the adhesive are accompanied by appearance of a tensile stress in the free edges of the adhesive in a direction normal to the glue line, causing a tendency toward peeling.

A compilation of the numerous designs developed for adhesive-bonded lap joints is shown in Figures 4 and 5. Selection among these joint designs is a compromise between strength and joint preparation cost. Similar principles of placing the glue line in shear can be applied in the design of other types of joints. Figure 6 shows some edge, angle, and tee joint designs. Sheet-metal corner joints usually require a third component, which may be a formed, machined, or extruded part. Tubular joints in hollow components should be designed using sleeves around the bond area or by sizing one adherend to fit within the other (Figure 7). Where butt joints must be made in thick materials, edges should be prepared so that a shearing component exists along at least part of the glue line, as shown in Figure 8. Similarly prepared faces having radial symmetry
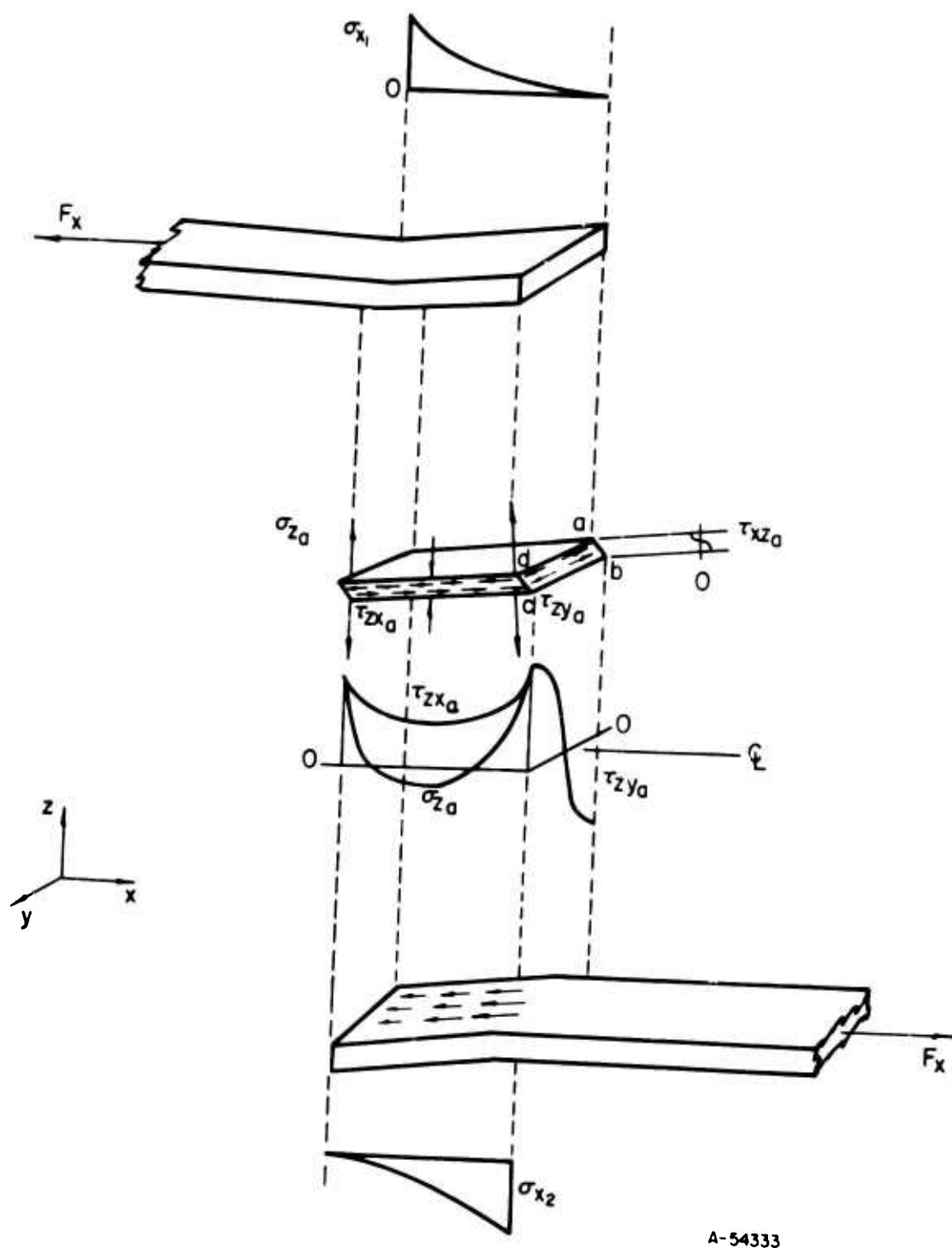
FIGURE 3. EXPLODED SCHEMATIC VIEW OF SIMPLE LAP JOINT SHOWING
DISTRIBUTION OF STRESS IN ADHESIVE AND ADHERENDS

A-54333

	Rigidity of Adherends	Stress Concentrations Under:		
		F	-F	M
Lap	$E_1 = E_2$	Major	Major	Major
	$E_1 > E$	Major	Major	Major
Beveled Lap	$E_1 = E_2$	Major	Major	Major
	$E_1 > E_2$	Moderate	Moderate	Major
Double Bevel Lap	$E_1 = E_2$	Minor	Minor	Moderate
	$E_1 > E_2$	Moderate	Moderate	Major
Relieved Lap	$E_1 = E_2$	Moderate	Moderate	Moderate
	$E_1 > E_2$	Moderate	Moderate	Major
Inset Lap	$E_1 = E_2$	Major	Minor	Major
	$E_1 \; E_2$	Major	Minor	Major
Beveled Inset Lap	$E_1 = E_2$	Moderate	Minor	Major
	$E_1 > E_2$	Moderate	Minor	Major
Reinforced Lap	$E_1 = E_2$	Major	Major	Major
	$E_1 > E_2$	Major	Major	Major
Intermediate Lap	$E_1 = E_2$	Moderate	Moderate	Major
	$E_1 > E_2$	Major	Major	Major

A-54365
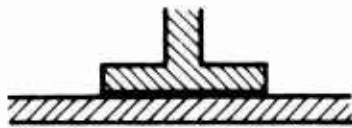
FIGURE 4.   SOME DESIGNS FOR OFFSET LAP JOINTS

(Partly from Ref. 42, Adhesive Bonding of Reinforced Plastics, by H. A. Perry, Copyright 1959, McGraw-Hill Book Co. Used by permission)

	Rigidity of Adherends	Stress Concentrations Under: F	-F	M
Butt	$E_1 = E_2$	Major	Major	Major
	$E_1 \cdot E_2$	Major	Major	Major
Scarf	$E_1 = E_2$	Minor	Minor	Major
	$E_1 > E_2$	Major	Major	Major
Offset Lap	$E_1 = E_2$	Major	Major	Major
	$E_1 \cdot E_2$	Major	Major	Major
Strap	$E_1 = E_2$	Major	Major	Major
	$E_1 > E_2$	Major	Major	Major
Double Strap	$E_1 = E_2$	Major	Major	Major
	$E_1 \cdot E_2$	Major	Major	Major
Recessed Double Strap	$E_1 = E_2$	Moderate	Minor	Major
	$E_1 \cdot E_2$	Major	Minor	Major
Beveled Double Strap	$E_1 = E_2$	Minor	Minor	Minor
	$E_1 \cdot E_2$	Moderate	Moderate	Moderate
Double Lap	$E_1 = E_2$, $E_1 \gg E_2$			
	$E_1 t_2 = E_1 t_2$	Major	Major	Moderate
Solid Double Lap	$E_1 \cdot E_2$, $E_1 \cdot E_2$	Major	Moderate	Major
	$E_1 t_1 = E_2 t_2$	Major	Minor	Moderate
Double Butt Lap	$E_1 = E_2$	Moderate	Minor	Major
	$E_1 \cdot E_2$	Major	Minor	Major
Double Scarf Lap	$E_1 = E_2$	Moderate	Minor	Major
	$E_1 \cdot E_2$	Major	Minor	Major
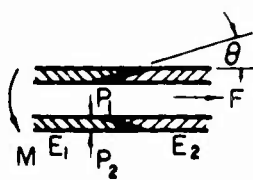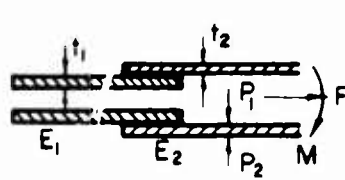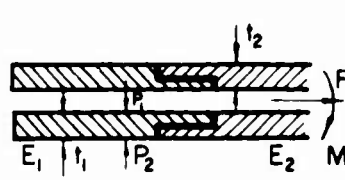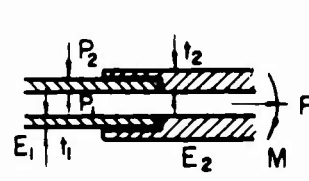
A - 54362

FIGURE 5.   SOME DESIGNS FOR COLINEAR LAP JOINTS
(Partly from Ref. 42, Adhesive Bonding of Reinfenced
Plastics, by H. A. Perry. Copyright 1959, McGraw-
Hill Book Co. Used by permission)

Corners and Angles		Tees	
Geometry	Efficiency	Geometry	Efficiency
	Poor		Good when unbeveled; excellent beveled
	Good		Poor without strap; excellent with strap
	Excellent		Poor without straps; excellent with straps
	Poor		Good without strap; excellent with strap
	Excellent		Good; excellent when beveled
	Fair		Good when unbeveled; excellent beveled
	Good		Fair

A-54363

FIGURE 6. SOME DESIGNS FOR EDGE, ANGLE, AND TEE JOINTS
(Partly from Ref 42, Adhesive Bonding of Reinforced
Plastics, by H. A. Perry, Copyright 1959, McGraw-
Hill Book Co. Used by permission)

Rigidity of Adherends	Stress Concentrations Under:				
	F	$-F$	$P_1 > P_2$	$P_2 > P_1$	M
$E_1 = E_2$	Minor	Minor	Minor	Minor	Minor
$E_1 > E_2$	Major	Major	Minor	Major	Major
$E_1 < E_2$	Major	Major	Major	Minor	Major
$\frac{E_1 t_1}{d_1} = \frac{E_2 t_2}{d_2}$	Major	Major	Minor	Minor	Major
$\frac{E_1 t_1}{d_1} > \frac{E_2 t_2}{d_2}$	Major	Major	Major	Minor	Major
$\frac{E_1 t_1}{d_1} < \frac{E_2 t_2}{d_2}$	Major	Major	Minor	Major	Major
$\frac{E_1 t_1}{d_1} = \frac{E_2 t_2}{d_2}$	Major	Minor	Minor	Minor	Major
$\frac{E_1 t_1}{d} > \frac{E_2 t_2}{d}$	Major	Minor	Major	Minor	Major
$\frac{E_1 t_1}{d_1} < \frac{E_2 t_2}{d_2}$	Major	Minor	Minor	Major	Major
$\frac{E_1 t_1}{d_1} = \frac{E_2 t_2}{d_2}$	Major	Minor	Minor	Minor	Major
$\frac{E_1 t_1}{d} > \frac{E_2 t_2}{d}$	Major	Minor	Major	Minor	Major
$\frac{E_1 t_1}{d_1} < \frac{E_2 t_2}{d_2}$	Major	Minor	Minor	Major	Major

A-54364

FIGURE 7. SOME DESIGNS FOR TUBULAR JOINTS
(Partly from Ref. 42, Adhesive Bonding of Reinforced Plastics, by H. A. Perry, Copyright 1959, McGraw-Hill Book Co. Used by permission)

26

Conventional Tongue and Groove

Landed Scarfed Tongue and Groove

Scarfed Tongue and Groove
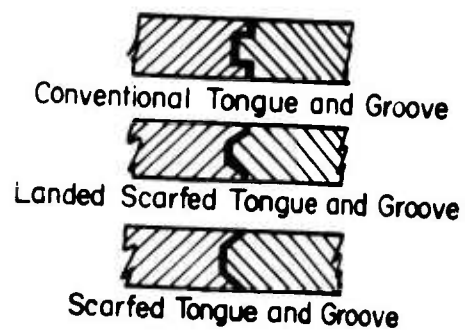
FIGURE 8. SOME DESIGNS FOR BUTT JOINTS (Ref. 27)

End lap

Mitered joint with spline

Mortise and tenon
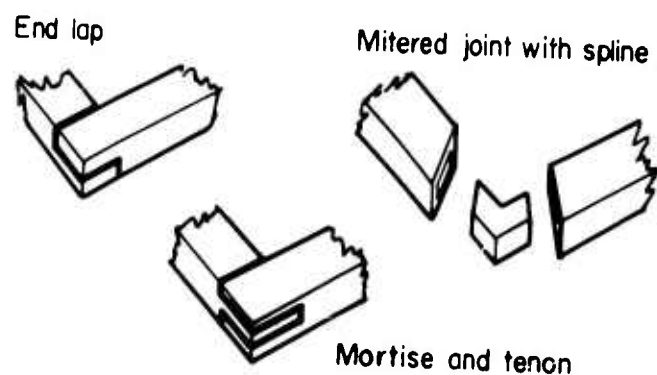
FIGURE 9. SOME DESIGNS FOR CORNER JOINTS (Ref. 27)

Rivet

A-54334

FIGURE 10. PEEL-RESISTANT DESIGNS FOR FLEXIBLE MEMBERS (Ref. 31)

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can be used when bonding solid rods. Some corner joint designs for beams
and struts are shown in Figure 9. Thin strips of bonded metal that are likely
to peel in flexure loading can be secured in several ways (Figure 10).

In adhesive-bonded skin-and-stringer panels, the designer has considerably
control over lateral stiffness of the joints through the use of doublers and
changes in details of the stringer cross sections, as shown in Figure 11.

Honeycomb-panel construction is becoming increasingly important as a
light-weight, rigid structural configuration. Such panels (Figure 12) have
been fabricated from wood, plastics, light metals, and ceramics by organic
and inorganic adhesive bonding, brazing, welding, and diffusion bonding. The
Armed Forces Supply Center has published a comprehensive handbook which covers
details of adhesive bonding of honeycomb (Ref.43). Figure 13 shows a variety
of edge-closure configurations that have been used with adhesively bonded
honeycomb panels.

Fabricating large honeycomb structures that require continuous-core
construction or sharp bends is difficult. Some techniques that have been
used in these cases are shown in Figures 14 and 15. Some methods of
attachment of panels are shown in Figure 16.

In some recent bonded honeycomb sandwich design, it has been necessary to
used a stepped skin (Figure 17). Herndon (Ref.47) has pointed out the desirability
of making the steps external if possible, rather than internal, from the
standpoint of obtaining a reliable core-to-skin bond. With internal skin steps,
the core must be contoured, and tolerance mismatches in layup are likely. These
will result in voids or crushed regions in the core. Although the figure shows
the external steps as being integral with the skin, they might also be bonded
doubler sheets.

28
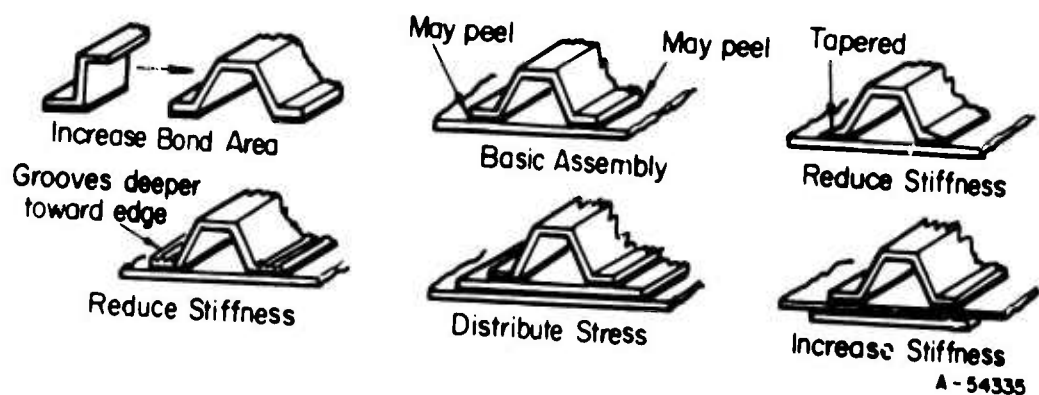
FIGURE 11.   SOME DESIGNS FOR HAT-SECTION SKIN-AND-STRINGER
CONSTRUCTION (Ref. 22)

29
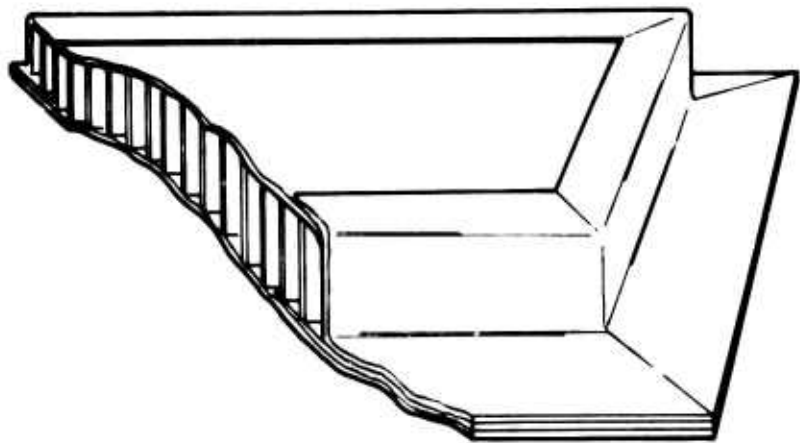
A-54336

FIGURE 12.   TYPICAL BONDED SANDWICH PANEL (Ref.44)

30
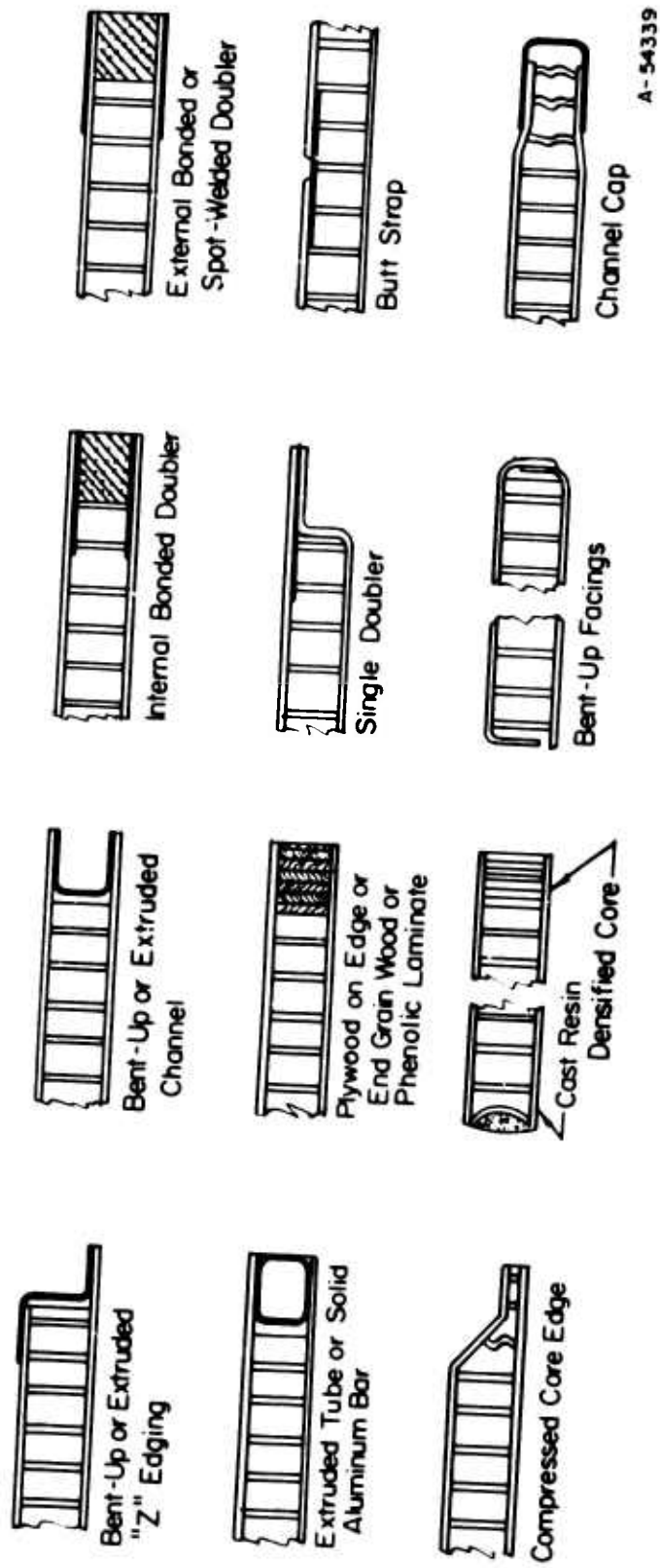
FIGURE 13. SOME DESIGNS FOR PANEL EDGE JOINTS (Ref.45)

31
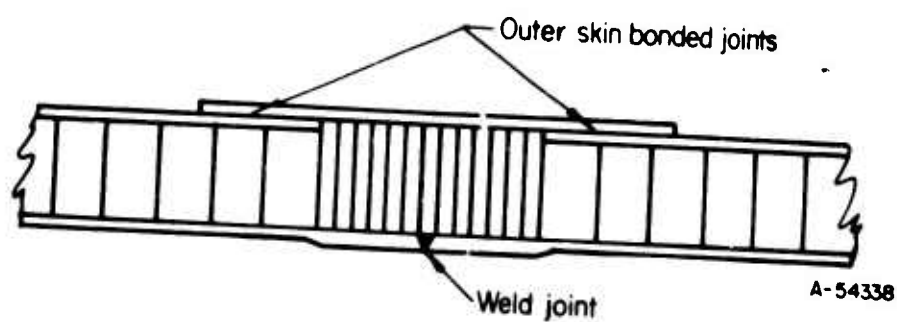
FIGURE 14.   CIRCUMFERENTIAL JOINT IN LARGE HONEYCOMB CYLINDER (Ref.46)

Normal core splice

Adhesive and foil sheet interlayers

A-54337
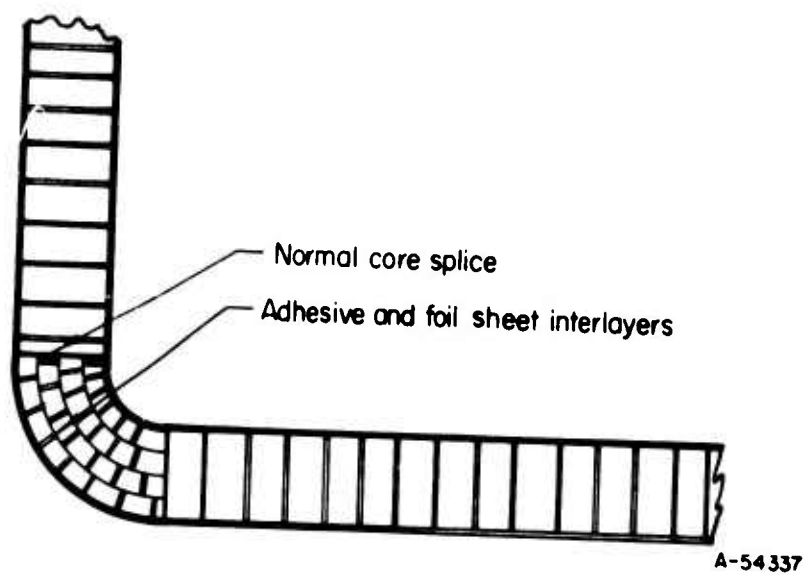
FIGURE 15.   DESIGN FOR A HONEYCOMB EDGE JOINT (Ref.44)

33

Standard fastener

Tubular spacer

Potting compound

Standard Fastener

Stepped Fastener

Integral Strip Insert

A-54340
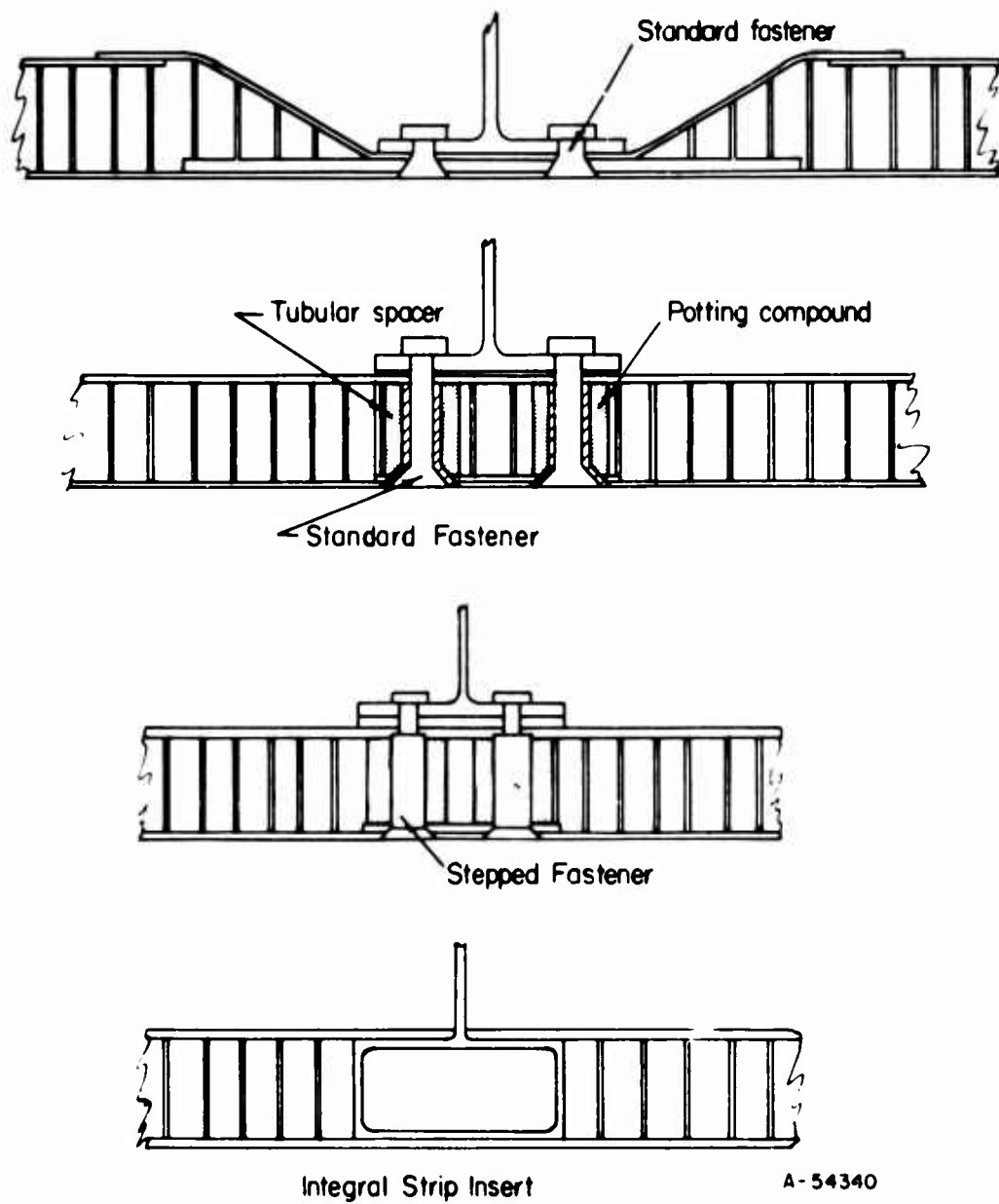
FIGURE 16. METHODS OF ATTACHING PANELS TO SUBSTRUCTURE (Ref.44)

34

Internal skin steps

External skin steps

A-54341
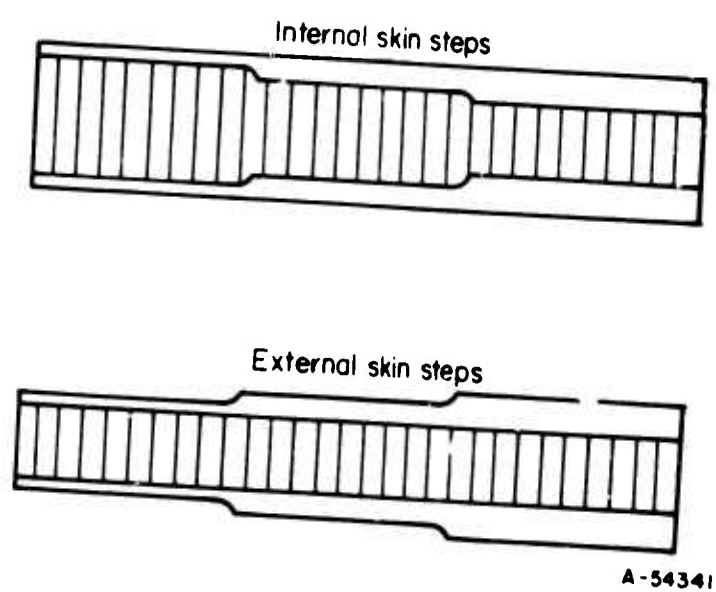
FIGURE 17.   INTERNAL VS. EXTERNAL SKIN STEPS (Ref.47)

When using some of the stronger adhesives with thin metal adherends in the metallurgically soft condition, cases have been encountered in which the bond apparently fails adhesively, that is, at the adhesive-adherend interface. Closer examination has revealed that the failure is not a result of poor adhesion, but is caused by mechanical yielding of the metal, with the consequent development of a large shear stress at the interface. The remedy for this type of failure is to change the metal to a heat-treated or cold-worked condition that has a higher yield point (Ref.48), to use a larger overlap, or to make the adherend thicker.

PREPARING THE ADHEREND SURFACES

Perhaps the most critical step in achieving a good adhesive bond is the preparation of the surfaces to be joined. Although it is frequently stated that the surfaces must be "clean", what is really meant is that certain types of contamination must not be present. This fact was not appreciated in some of the early work with metal-to-metal adhesive bonding, and many bond failures that were attributed to poor adhesion are now believed to have resulted from the presence of a mechanically weak surface film on the metal.

Figure 18 shows the sequence of operations common to most adherend preparation processes.

For Inorganic Adhesives

Step 1. Degrease

Step 2. Acid Etch or Alkaline Clean

Step 3. Rinse

Step 4. Dry

Step 5. Condition Surface

Step 6. Rinse

Step 7. Dry

Step 8. Prime or Bond

Step A. Heat Scale

Step B. Sandblast, Vapor Hone, or Etch

Step C. Degrease (Omit if Etched)
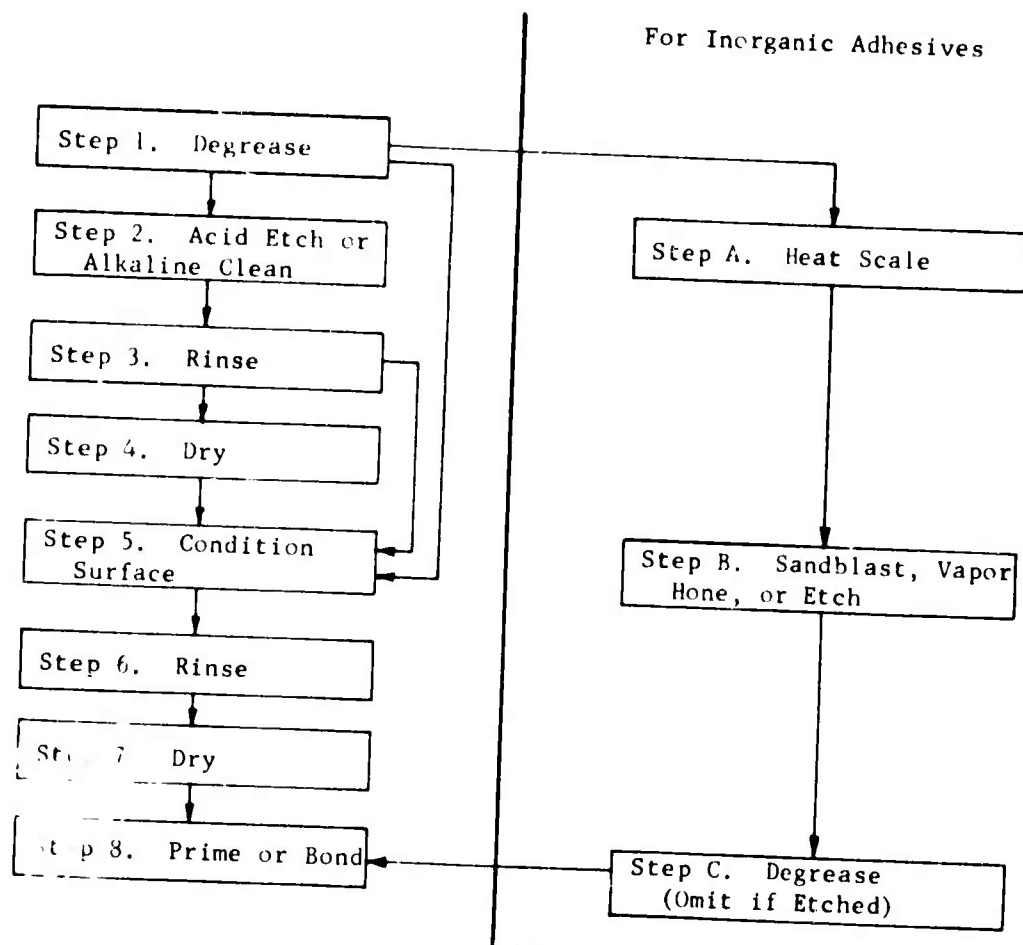
FIGURE 18. GENERALIZED FLOW CHART OF ADHEREND SURFACE-PREPARATION PROCESSES

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Step 1. Degrease. Degreasing is common to all processes and usually employs a chlorinated solvent such as trichloroethylene. Other solvents, such as acetone, methylethyl ketone, carbon tetrachloride, isopropyl alcohol, xylene, toluene, and perchloroethylene, can be used with proper regard for their flammability, toxicity, and cost. Parts may be immersed, vapor degreased, or swabbed with solvent-moistened cloths.

Vapor-phase degreasing removes contamination by a refluxing action in which the pure solvent vapor condenses on the cold workpiece, dissolves the contaminants capable of solution, and drips off the workpiece. This action ceases when the workpiece reaches the vapor temperature, and it serves no purpose to leave the workpiece in the degreaser for longer times.

When using the solvent-wiping technique, often necessary when the pieces to be bonded are large, it is important to use clean, soap-free cloths, plenty of oil-free solvent, and to wipe the solvent off the surface before it has time to dry.

Step 2. Acid Etch or Alkaline Clean. The next step is to remove any visible oxide film or scale by a pickling or acid-e   ing treatment or to r move any organic material with an alkaline cleaning solution. Whether either of these treatments is necessary depends upon the history of the adherend. They may be omitted for a cold-finished mill product if tests indicate no improvement in adhesive-joint properties from their use. Many of the cleaning solutions used are proprietary, and manufacturers' instructions should be followed concerning their use. For large parts which require the wipe-on process, mechanical abrasion with an abrasive pad or fine-grit paper has been substituted for this step in the procedure (Ref. 46).

Step 3. Rinse. Opinions differ as to whether water rinses should be hot or cold; tap, demineralized, or distilled water; immersion or spray; or whether the hot rinse should precede the cold. Rider (Ref. 49) recommends that

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electrical conductance of water to be used for a spray rinse be less than 10 microhms, water for a tank rinse be less than 30 microhms, and warns that water in many plants contains organic materials. To determine whether tap water in a given locality can be used for rinsing, long-term strength retention tests should be made of adhesive bonds made using tap-water-rinsed adherends as compared with similar bonds made using organic-free distilled water. Use of tap-water rinsing is not recommended, however. The impurity levels in tap water, even from a single source, are not subjected to long-term control and may be responsible for apparently random time periods during which bond strengths produced are below specification. The objective of any rinsing procedure is the complete removal of the etching or cleaning solution as indicated by neutrality of the effluent rinse water (pH = 7). Presence of residual etching or cleaning solutions may cause corrosion of the adherends and may affect the adhesive chemically.

Step 4. Dry. Few processes include this drying step, preferable practice being to proceed directly to the surface-conditioning step following the rinse. If it is necessary to dry the workpiece after Step 3, it should be done in air as clean, still, and dust free as possible, or drying can be forced using a clean, warm air blast or a circulating oven.

Step 5. Condition Surface. In the surface-conditioning step, a corrosion film of controlled chemical composition and thickness is deliberately formed on the adherend surface. Surface roughness is also modified, and if the operation is properly carried out, any microscopic subsurface contamination pockets that might have been rolled into the surface during mill processing are exposed and removed. Typically, the films used are complex mixtures of phosphates, fluorides, chromates, sulfates, or nitrates. The composition of the film may be the most important single factor controlling the strength of the adhesive-bonded joint under the desired service conditions. Evidence suggests that some film compositions and thicknesses are markedly superior to others, especially at ex-

tremes of service temperatures. No systematic study has been published of the influence on joint properties of film compositions and thicknesses as functions of solution composition, treatment time and temperature, and alloy. The approach has instead been empirical, which is understandable considering the complexity of the relationships and the experimental difficulties in characterizing the films. Until more fundamental information is available, the user must choose among possible surface-conditioning processes on the basis of tests made using his parts bonded and tested under simulated service conditions.

Steps 6 and 7. Rinse and Dry. Statements made under Steps 3 and 4 apply here also.

Step 8. Prime or Bond. Metals differ in the rate at which atmospheric oxygen and moisture will reform a sufficiently thick film on the metal surface so that the value of the surface preparation is lost. For example, copper and brass should be bonded immediately after cleaning. Bonding of aluminum can be delayed a half hour after cleaning. For titanium, an elapsed time no greater than 8 hours between cleaning and bonding is recommended. Stainless steels have been successfully bonded days after cleaning. The longer the time, however, the more the likelihood of organic contamination from handling, from airborne liquids or solids, or from accidental causes, or of mechanical damage to the surface film. Best practice, therefore, is to bond immediately after surface preparation. If this is not possible, the prepared surfaces should be primed according to the adhesive manufacturer's directions and the parts stored in a clean, dry place, preferably protected by a cover of some sort, until ready for bonding. Handling of cleaned parts should be done only using clean cotton or nylon gloves.

Reported Surface Preparation Procedures for Bonding Stainless Steels With Organic Adhesives. Mechanical abrasion and chemical treatments have both been used for preparing stainless steel surfaces for adhesive bonding. The Ameri-

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can Society for Testing and Materials tentatively recommends the mechanical treatment--sand blasting, grit blasting, or vapor honing--of previously degreased parts as the preferred surface treatment (Ref. 50). Following the abrasion step, surfaces must be washed, brushed, or blasted with an oil-free air or nitrogen jet to remove abrasive and metal dust. The Minnesota Mining and Manufacturing Company uses a trichloroethylene rinse (Ref. 51). Bonding should be done as soon as possible following surface preparation. The tentative ASTM procedure would substitute a chemical method of surface preparation only for adherends that are so thin that they would be distorted by the forces involved in the mechanical treatment. On the other hand, Hill (Ref. 52) reports superior tensile-shear strengths with polybenzimidazole adhesive on 17-7 PH stainless steel using a chemical treatment (G in Table III), when directly compared with a wet grit-blasting treatment.

Bell Helicopter Company uses a sulfuric acid chemical treatment, both because their parts are thin and because they can control the chemical process more accurately than a mechanical process. They also buy their stainless steel heats on the basis of a bondability acceptance test (Ref. 53).

Lockheed has been successful in achieving high-strength bonds in both stainless steels and titanium with the same alkaline cleaner. They believe that the alkali, if incompletely rinsed, is less likely to degrade an adhesive than an acid would. They have not observed any stainless steel heats that were not bondable (Ref. 54).

Table III summarizes the various chemical surface treatments that have been reported for stainless steels. One often finds slight compositional variations in the reagents as reported by different investigators, but an attempt has been made in the table to include representative recipes for the different baths reported.

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TABLE III. SURFACE PREPARATION PROCEDURES FOR STAINLESS STEELS PRIOR TO BONDING WITH ORGANIC ADHESIVES

| | | | | | Process Step | | |
Procedure	Degrease	Clean/Etch	Rinse	Dry	Surface Condition	Rinse	Dry
A(Ref.55)	--	--	--	--	10 wt % H_2SO_4 10 wt % oxalic acid 80 wt % H_2O Temp 60-95 C Time 30-10 min	Cold H_2O	--
B(Ref.55)	--	--	--	--	46 wt % HCl 2 wt % H_2O 10 wt % formalin 42 wt % H_2O Temp 60 C Time 10 min	Cold H_2O	--
C(Ref.55)	--	--	--	--	81 vol % HCl 19 vol % H_2O Temp 20 C Time 15 min	Cold H_2O	--
D(Ref.56)	Trichloroethylene 10 min at RT or vapor degrease 10 min at 180-190 F	--	--	--	A 94.4 wt % H_2O 2.0 wt % Na_2SiO_3 (metal) 3.6 wt % Triton X200 or B 96.6 vol % H_2SO_4 3.4 vol % saturated $Na_2Cr_2O_7$ solution Temp 150 - 160 F Time 15 min	Tap water 180-200 F Demineralized water 180-200 F or RT	Air; oven if RT rinse;<200 F
E(Ref.3)	MEK:TCE	55 parts/wt Na_2SiO_3 (meta) 35 parts/wt tetra sodium pyrophosphate	10 vol % HCl 90 vol % H_2O	--	100 parts/wt H_2O 40 parts/wt H_2SO_4	Tap water Distilled water spray	Oven 10-15 min 200 F

TABLE III. (CONTINUED)

			Process Step				
Procedure	Degrease	Clean/Etch	Rinse	Dry	Surface Condition	Rinse	Dry
E(Ref.3) Cont'd.	MEK;TCE	5 parts/wt Nacconal NR 15 parts/wt NaOH 2400 parts/wt H_2O Temp 165-185 F Time 5-10 min	--	--	0.5 parts/wt Nacconal NR Temp 150-160 F Time 5-10 min H_2O rinse 100 parts/wt H_2O 20 parts/wt HNO_3 2.5 parts/wt HF RT Time 5-10 min	Tap water Distilled water spray	Oven 10-15 min 200 F
F(Ref.3)	MEK;TCE	--	--	--	25 parts/wt hexa-methylene tetramine 100 parts/wt H_2O 10 parts/wt HCl 5 parts/wt 30 per cent H_2O_2 Temp 150-160 F Time 5-10 min	--	--
G(Ref.3)	MEK;TCE	--	--	--	80 parts/wt HCl 8 parts/wt H_3PO_4 4 parts/wt HF Temp 180-190 F Time 1-2 min	Tap water Distilled water spray	Oven 10-15 min 200 F
H(Ref.57)	TCE	4 vol % H_2SO_4 4 vol % HCl 92 vol % H_2O Temp Time 20 min	--	--	12 vol % HNO_3 2 vol % HF 86 vol % H_2O Temp Time 15 min	Water	--
I(Ref.49)	--	--	--	--	50 vol % HCl 50 vol % H_2O Temp Room Time 5-10 min	Deionized water 200 F max	Oven 200 F
J(Ref.58)	TCE;CCl_4	--	--	--	90.4 wt % H_2O 6 wt % Na_3PO_4 3.6 wt % Triton X200	Cold H_2O	--

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TABLE III. (CONTINUED)

			Process Step				
Procedure	Degrease	Clean/Etch	Rinse	Dry	Surface Condition	Rinse	Dry
K(Refs.59,60)	Scrub w/MEK; Dry; Vapor degrease 10 min in TCE	**A** 7-17 vol % HNO_3 6-9 oz/gal Ammonium Bifluoride H_2O to one gal. Temp 130-150 F Time 20 sec or **B** 170 ml 70 % HNO_3 59.5 gm MF Acid H_2O to one liter Temp 130-150 F Time 12 min	Tap water	--	30 pbw H_2O 10 pbw H_2SO_4 1-4 pbw $Na_2Cr_2O_7$	Tap water; Distilled water spray	Oven 155-165 F
L(Ref.61)	Acetone wipe; Water rinse	Prebond 700 Temp 200 F	--	--	**A** 4 vol % H_2SO_4 4 vol % HCl 92 vol % H_2O Temp Time 20 min followed by **B** 12 vol % HNO_3 2 vol % HF 86 vol % H_2O Temp Time 15 min	Water	Air dry 150 F

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Meckelburg, Schlothauer, and Neumann (Ref. 55) studied a variety of surface-preparation processes for stainless steels and reported that the three identified in the table as A, B, and C resulted in the highest tensile-shear-strength adhesive bonds. They also noted, however, that sandblasting or simply degreasing in carbon tetrachloride gave almost equivalent results. Guttman (Ref. 3) lists four procedures (D through G) for stainless steels, the first (D) also recommended by Lindsay (Ref. 56). The procedures given in G and K have been used on PH 15-7 Mo precipitation-hardening stainless steel.

A powdery surface deposit, or smut, frequently forms on stainless steels during chemical treatment. The smut can usually be scrubbed off, or, according to Rogers (Ref. 62), can be chemically removed with a 25% H_2SO_4-2.5% $N_2Cr_2O_7$ solution at 160 F. The precipitation-hardening stainless steels are said to be more prone to smut formation than the conventional stainless steels.

In setting up a surface preparation procedure for critical structural joints, one should try one or more candidate procedures, select one on the basis of comparative joint strength tests, and then vary bath compositions and process parameters to optimize joint strength.

Compromises. Relaxing of the surface-preparation requirements must be done cautiously, because some very subtle factors may cause an unexpected loss of bond strength. Bikerman (Ref. 2) suggests that surfaces may actually be contaminated by a sandblasting operation if the sand contains organic matter, as is often the case if the sand has not been prebaked. He also cites results by other investigators that show a 50 percent loss in adhesive bond strength due to 0.1 microgram of decanoic acid (a material similar to a perspiration film) per square centimeter of adherend surface. When beginning work with a new material, the user probably will save time and money in the long run if he will use moreelaborate procedures than he believes are necessary and will then work toward their simplification, instead of the other way around. This is true even if the user is experienced in the art of adhesive bonding.

Tests for Proper Surface Preparation. The so-called water-break test, which can be used at any stage of the cleaning procedure, is the simplest and most widely used method of determining surface cleanliness. If a drop of distilled water wets the metal surface and spreads, or if a film of distilled water on the surface does not break up into individual droplets, the surface can be presumed to be free of harmful organic films. A surface which is uniformly wet by distilled water will probably also be wet by the adhesive.

A drop of an organic solvent has sometimes been substituted for the drop of water. This is not a suitable test, since the organic solvent may have the power of dissolving any organic film present and then wetting the surface. Thus it would not indicate presence of the contaminant.

It should be emphasized that satisfactory wetting of the surface in the water-break test merely shows whether the surface energy of the metal (which may still be coated with a hydrophilic film) is higher than that of water. It gives no information concerning the strength of any film present and, therefore, is not a test of attainable adhesive-bond strength. A satisfactory waterbreak test is at best a necessary, but not a sufficient, requirement for high bond strengths.

SELECTING THE ORGANIC ADHESIVE

Because of the large number of organic compounds, it is not surprising to find that there are hundreds of commercially available adhesives. Although these substances fall into a limited number of chemical categories, it is probably safe to say that no two adhesives manufactured by different companies are precisely alike. For example, each of the many different curing agents for epoxy resins imparts something of its own characteristics to the adhesive. Innumerable variations are possible in details of resin chemistry and blending, and the industry pattern is that detailed information concerning adhesive compositions is usually proprietary with the adhesive manufacturer. For these reasons un-

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satisfactory performance of one manufacturer's adhesive in an application cannot be interpreted as an indication that no adhesive of that class can be used. The unsatisfactory behavior may be due to some detail of the user's bonding process to which another adhesive might not be so sensitive. A good example might be high sensitivity of one adhesive to alkalinity of a poorly rinsed adherend surface, while another adhesive may be relatively unaffected. Two or three promising adhesives should therefore be tried for a new application if there is any uncertainty of results.

The adhesives that are most useful for structural adhesive bonding belong to the class known as thermosetting adhesives. These adhesives undergo chemical changes during the curing cycle which render them incapable of being dissolved in the common solvents or melted. They tend to char when overheated. Chemically, the change during curing consists of the formation of crosslinkages between resin molecules to form three-dimensional polymer networks. Thermosetting adhesives are the strongest class of adhesives and the only class worthy of consideration for high-temperature applications.

Adhesive Tests. In this report, comparisons of bond strengths will be made on the basis of simple overlap tensile-shear tests. Although other types of tests are necessary to evaluate an adhesive completely, and may even be preferable from a theoretical standpoint (Ref. 63), the simple lap joint pulled in tension is easy to make and test and provides meaningful comparative results. Dimensions of the tensile-shear specimen have become generally accepted as set forth in Federal Test Method No. 175, Tentative Standard Method 1033.1-T. A sketch of the test specimen is shown in Figure 19. All tensile-shear results mentioned in this report were obtained using specimens having dimensions shown in the sketch unless otherwise noted.
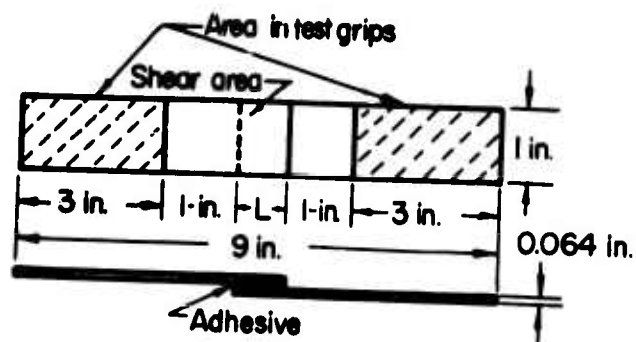
$L_{max} = \frac{Yt}{r}$ in.,

Where Y = adherend yield strength, psi
t = adherend thickness, in.
$r = 1.5 \times$ estimated adhesive shear strength, psi

L is usually taken as 0.5 in. for metal adherends.

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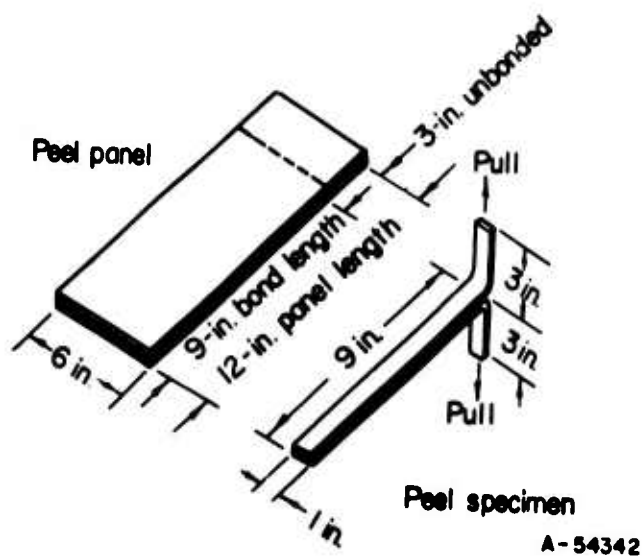
FIGURE 20.   CONFIGURATION OF PANEL AND INDIVIDUAL TEE-PEEL TEST
SPECIMEN (REF. 64)

Another type of mechanical test that is sometimes used in adhesive evaluation is the tee-peel test, one specimen for which is shown in Figure 20. This test is not covered by Federal Test Method No. 175. It is apparent that adherend material and thickness can influence the results of this test, which are reported in terms of strain energy per unit width of specimen, in-lb/in.

A third type of test, referred to as the pi-tension test, 's one in which two circular blocks of the adherend metal are bonded with the adhesive under test and then pulled in tension normal to the bond plane. This test is covered by Federal Test Method No. 175, and sketches of the adherend block and the testing arrangement appear in Figure 21. This test has been adapted for testing adherence of honeycomb-panel cover sheets to core. Circular portions of the cover sheets opposite each other are first isolated from the rest of the cover sheets using a fly cutter. They are then bonded to blocks, and the entire assembly is pulled in tension. Results will be influenced by the details of core configuration, so this is a specialized test.

Figures 22 and 23 show the specimen design and test fixture for determination of the shear modulus of an adhesive. Lunsford (Ref. 65) discusses the use of this test and the design significance of the modulus values obtained, as well as design testing of honeycomb panel specimens. Two relatively simple test specimens have been used at General Dynamics/Fort Worth to generate panel edge fitting design data (Figures 24 and 25) by varying the ratio between the overlap test length and the core thickness, L/T. It has been found that use of the compression L/T specimen gives higher strength values than the tension specimen.

Reed and Marano (Ref. 66) have shown that for polybenzimidazole adhesives tested at high temperature, the perimeter of the bond, or the amount of adhesive exposed directly to air is a joint design factor of equal importance with the L/T ratio and the adhesive shear modulus.

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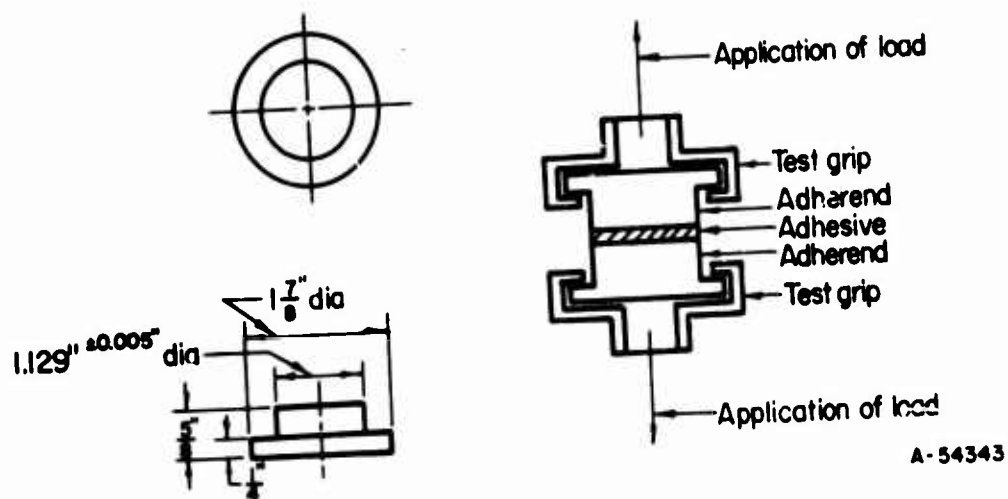
FIGURE 21.   ADHEREND BLOCK AND TESTING ARRANGEMENT
             FOR PI-TENSION TEST

             From Federal Test Method No. 175, Method 1011.1.
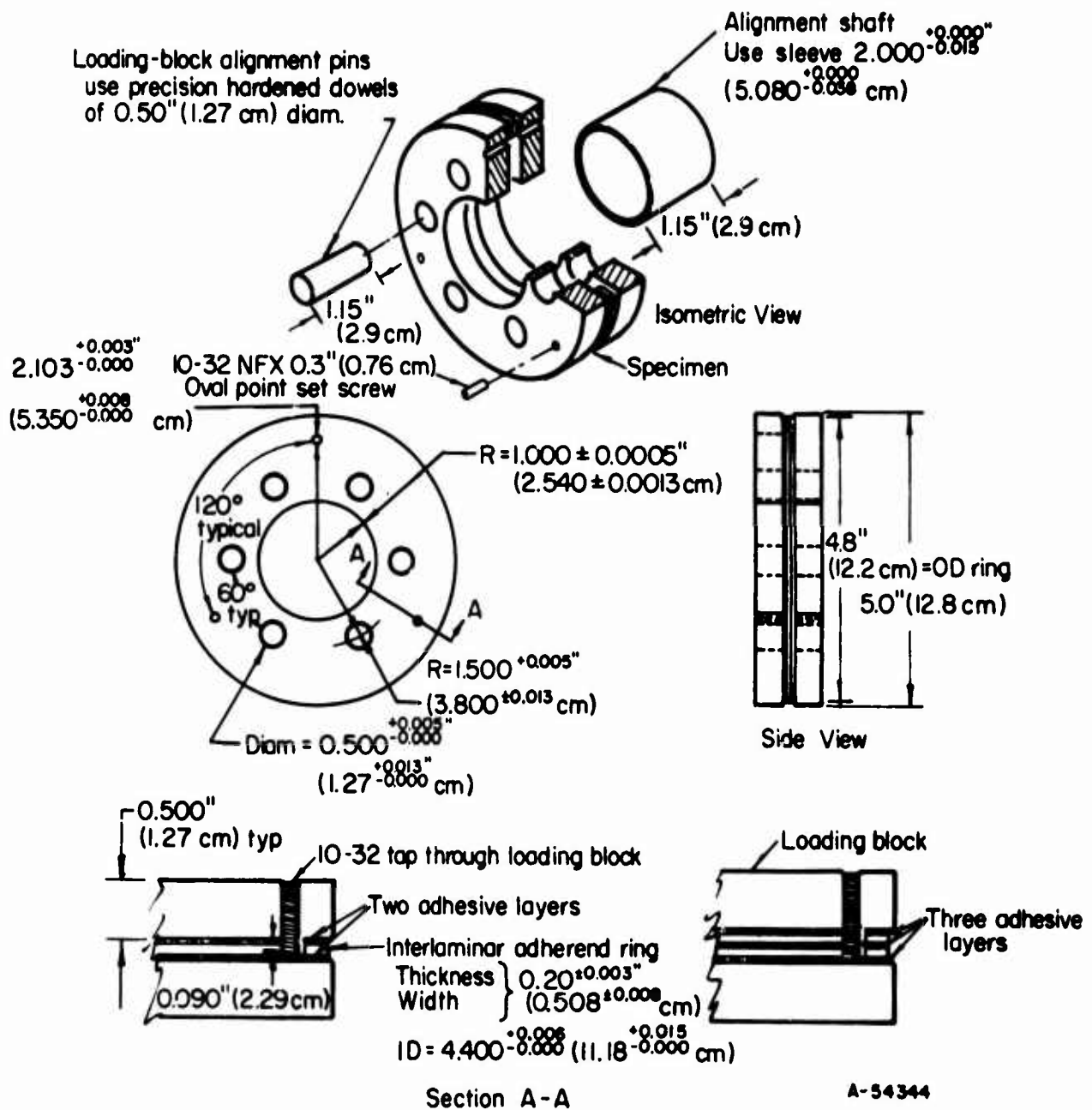
FIGURE 22. ADHESIVE TORSIONAL SHEAR SPECIMEN AND
ALIGNMENT SETUP (REF. 65)
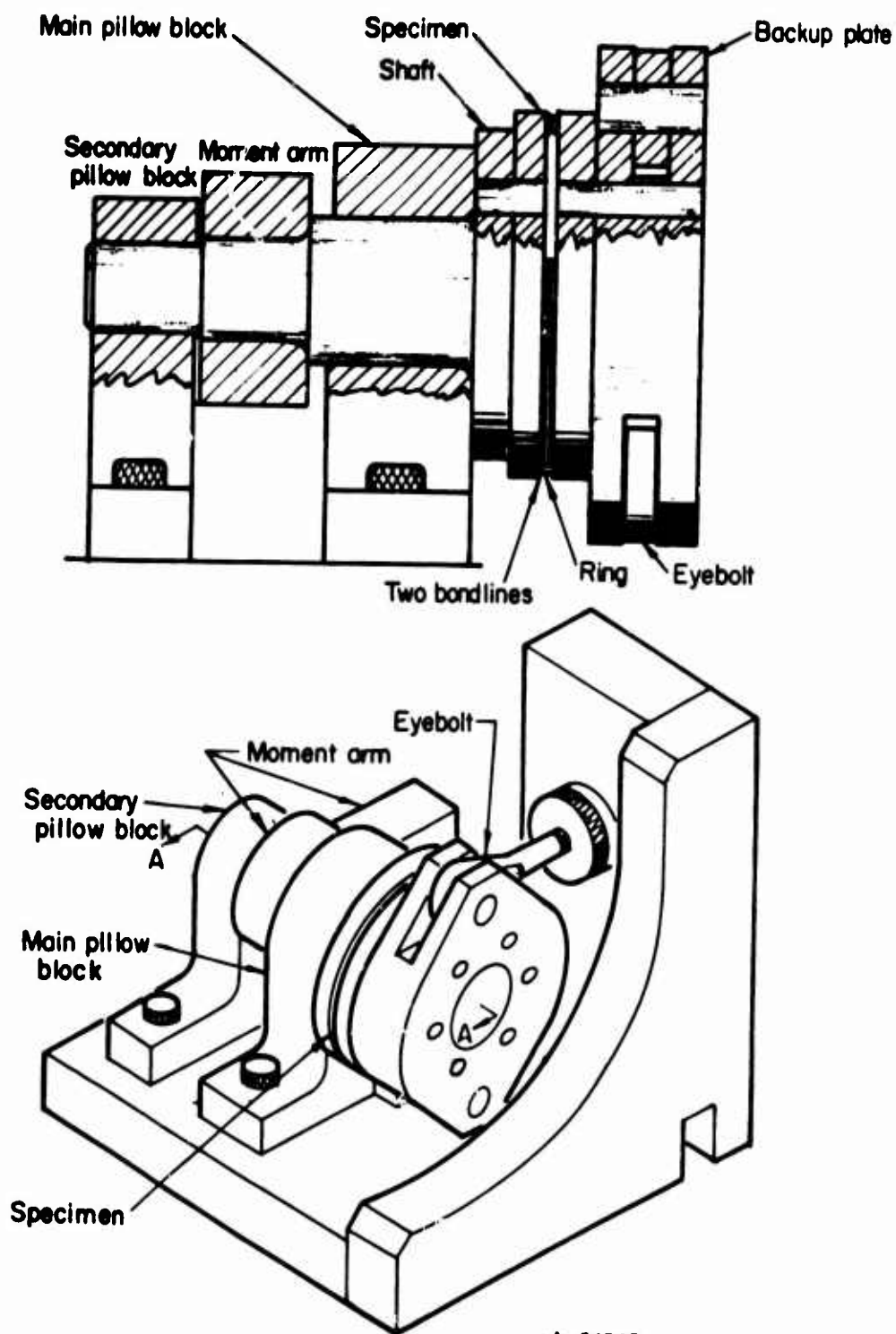
FIGURE 23. TORSIONAL SHEAR JIG (REF. 65)

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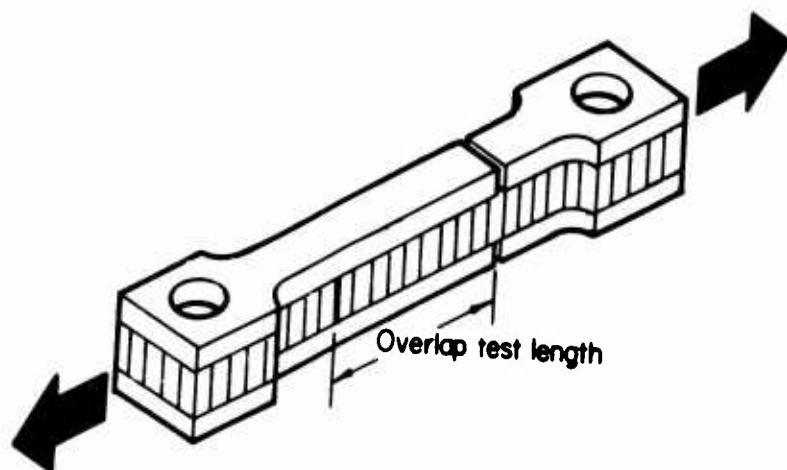
FIGURE 24. OVERLAP COMPRESSION TEST SPECIMEN
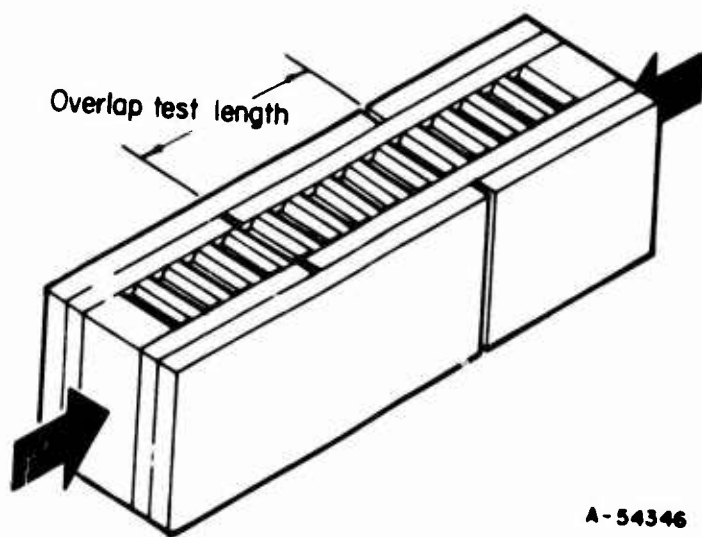
A-54346

FIGURE 25. DOUBLE OVERLAP COMPRESSION TEST SPECIMEN
(REF. 47)

General Dynamics' Portashear test has been used as a production quality control test on bonded panels (Figures 26 and 27). Although in the test a circular piece of the face sheet is sheared losse from the core, the damaged region is small and can be patched. A direct measure of bond strength achieved in production can thus be obtained without destroying the panel.

Other mechanical tests applied to honeycomb include the climbing-drum peel test (covered by Federal Test Method No. 175), and various forms of tests in which honeycomb panels are loaded as 3-point and 4-point beams, in flatwise compression, and in edgewise compression, tension, or shear. A detailed study of these tests is beyond the scope of this report, however, some information concerning them will be found in Reference 33.

Adhesive Standards and Specifications.   Guttman (Ref. 3), Katz (Ref. 7), and Licari (Ref. 67), have summarized or reproduced in their entirety the numerous Government, military, and industry-wide specifications relating to adhesive bonding.

Physical Forms of Adhesives Packaging.   Metal-bonding adhesives are most commonly used as liquids, films, or tapes. Some of the thicker liquids are thixotropic*, which is an aid in maintaining proper positioning of adherends following adhesive application, but prior to curing.

Adhesive films and tapes, either unsupported or supported on a carrier, are attractive for production operations because of easy control of bond-line thickness and convenience of handling. The form in which the adhesive is used in a particular application will depend upon the joint area to be bonded, the production volume, the types of equipment on hand, and the available forms of the adhesive to be used.

Most of the two-part liquid adhesives used in industrial quantities are shipped in cans or drums. A wide variety of equipment is available commercially that can meter and proportion the resin and hardener as desired, mix them, and dispense the mixture.

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* Thixotropic materials are viscous if allowed to stand undisturbed, but decrease in viscosity temporarily following stirring or other agitation. On standing, they revert to their former gelled state.

Detail of Portashear
test mechanism
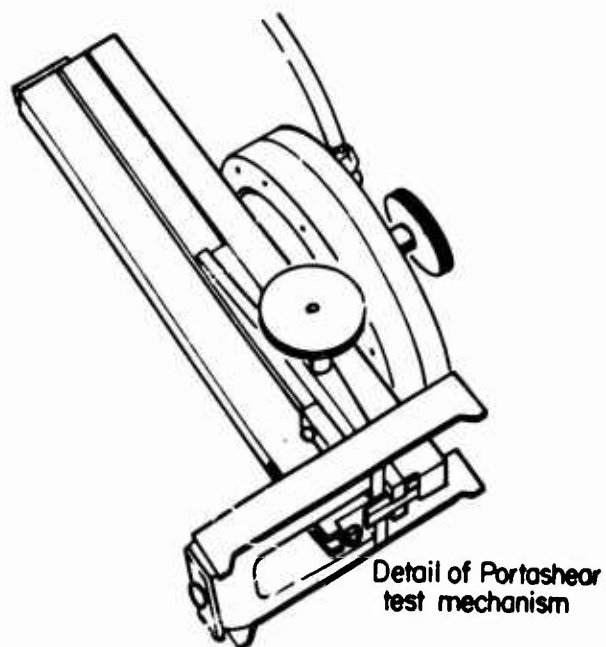
FIGURE 26. SCHEMATIC DRAWING OF PORTASHEAR SHEAR
MECHANISM

Shear force

reaction

Clamp

Clamping motion
expands reaction
hoop in specimen

Before test

After failure

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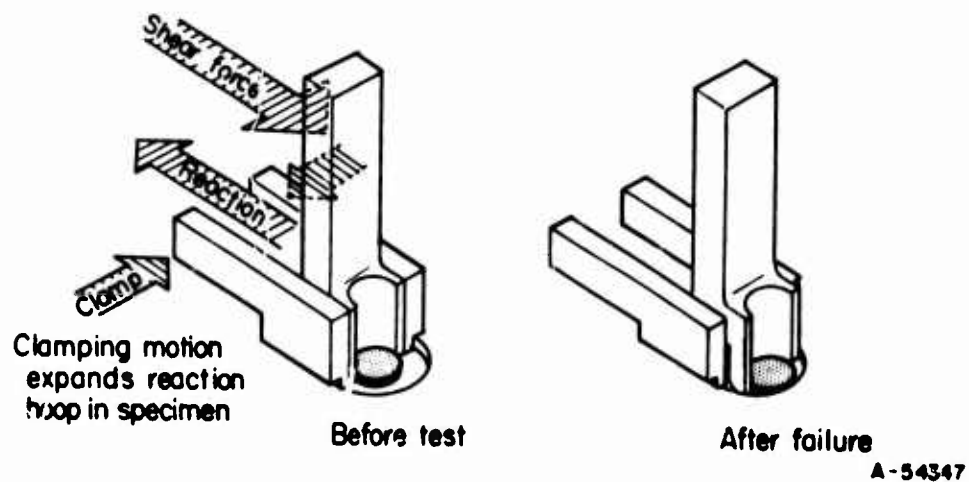
FIGURE 27. SCHEMATIC DRAWING OF PORTASHEAR SHEAR
MECHANISM (REF. 65)

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Two-part epoxy adhesives are being packaged in small quantities in separate collapsible tubes with extenders in the hardener so that one squeezes out equal lengths of material from each tube and mixes them with a spatula on a clean surface, such as glass.* Thorough mixing is often assured by coloring one of the components and mixing until the color of the resin-hardener mixture is uniform.

A more convenient method of packaging two-part adhesives in small quantities is the use of a two-compartment flexible plastic container. The container is so designed that the compartment divider can be ruptured by manual pressure, allowing the premeasured quantitites of resin and hardener to come in contact. Mixing is accomplished by kneading the package, after which the package is opened and the adhesive is dispensed.

A popular packing method for silicone sealant adhesive as a one-part liquid is based on the evaporation of a volatile chemical blocking agent after the adhesive is exposed to air. Departure of the blocking agent permits the resin-hardener reaction to occur.

Development is under way for mechanically blocked packaging systems, in which the hardener is held suspended and dispersed in the resin within molecular sieve particles or microcapsules that can be ruptured by heat or mechanical pressure.

Working and Storage Requirements. Prior to mixing, many two-part epoxy adhesives, consisting of resin and curing agent, can be stored at room temperature almost indefinitely. Once mixed, however, they have working times of only minutes or hours, depending upon the ratio of resin to curing agent and the specific curing agent used. The adhesives must be applied during the working time or the cure will have progressed to the point that the resins may be too stiff to

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* Use of organic films, such as Cellophane, as mixing surfaces is not recommended. Cases are known where chemicals from such films have been absorbed by adhesives, causing a loss in bond strength.

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apply. Two-part epoxies have the advantage that they can be cured at room temperature, thus requiring no curing ovens, autoclaves, or heated presses. Their properties are generally inferior to those of heat-cured epoxies, however, unless they are given an elevated-temperature postcure.

One-part epoxies and phenolics generally must be cured at elevated temperatures, although a room-temperature-curing epoxy film adhesive has recently become available. The former are compounded mixtures of resin and curing agent and have a limited shelf life. Usual shelf life of present commercially available one-part epoxies and phenolic adhesives is from 6 months to a year at room temperature. Shelf life can be extended if the adhesives can be stored in a freezer or refrigerator. The recently developed film adhesive mentioned above has very limited room-temperature working life and is shipped from the manufacturer to the user under dry-ice refrigeration.

Cans of adhesives and curing agents, once opened, should be used as quickly as possible or tightly reclosed and returned to storage in a cool place. Curing agents should be ordered with, and used with, specific batches of adhesive. Use of adhesives from storage should be on a first in-first out basis, and outdated adhesives should be discarded or should not be used without at least first making bond-strength measurements to insure that they have not deteriorated. Users of large quantities of adhesives make simple quality assurance tests on their ad-hesives (such as tensile shear and tee-peel, for example) at frequent intervals to eliminate the possibility of off-specification adhesives being used in their manufacturing operations (Ref. 68).

Service Conditions. No single adhesive is available that is superior for all service conditions. A user therefore makes a selection among possible adhesives on the basis of known or anticipated service conditions for the application.

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High Temperature. Strengths of adhesives, like strengths of metals, decrease with increasing temperature (Figure 28). It is difficult to state precise upper limits for service temperatures of the various types of adhesives. The limiting temperature depends on the anticipated service life, the metals being bonded, the magnitude and state of stresses imposed, and the presence or absence of deleterious environmental factors such as oxygen and radiation.

Several helpful review articles have recently appeared dealing with high-temperature adhesives (Refs. 69-71). It is generally observed that the same adhesive will give different tensile-shear-strength values when used to bond different adherends. It is therefore dangerous to assume without making tests that strength values reported for bonds are valid when made using adherends other than the stainless steel of interest. Additional variables influence the bond strength, among them surface treatments and degradation reactions.

At elevated temperatures, strengths of adhesive bonds generally decrease with time (Figure 29). Over some ranges of temperature, and depending on prior curing conditions, bond strength may increase with time for awhile (Figure 30). The general trend, however, is towards progressive loss of strength with time, the loss occurring at increasing rate with increasing temperature.

Atmospheric oxygen attack has been identified as being among the most important mechanisms by which organic adhesives degrade at high temperatures. Figure 30 shows the behavior of one adhesive at 600 F in air and in nitrogen, for example.

Thermal Catalytic Degradation. An adhesive-bonded joint must be thought of as a dynamic system consisting of an adhesive polymer molecule/adherend constituent cations/atmospheric oxygen and water vapor. Recognition of the dynamic nature of the bond is particularly important for high-temperature applications. Under the influence of heat, reactions tend to take place that include cracking of the adhesive molecules, evolution of low molecular weight, volatile reaction products, and diffusion of metal ions, oxygen, and water vapor into the adhesive.

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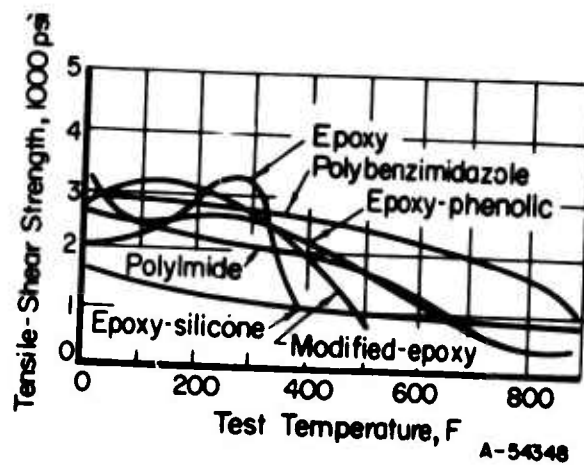
FIGURE 28. TEMPERATURE DEPENDENCE OF SHORT-TIME TENSILE-SHEAR STRENGTHS OF VARIOUS CLASSES OF ADHESIVES (REF. 69)

Adherends unspecified.
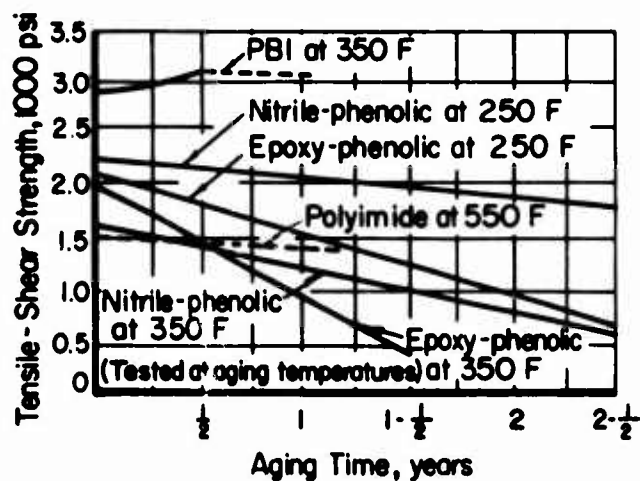
FIGURE 29. EFFECT OF TIME AT TEMPERATURE ON TENSILE-
SHEAR STRENGTHS OF JOINTS BONDED WITH
VARIOUS ADHESIVES (REF. 69)

Adherends unspecified.
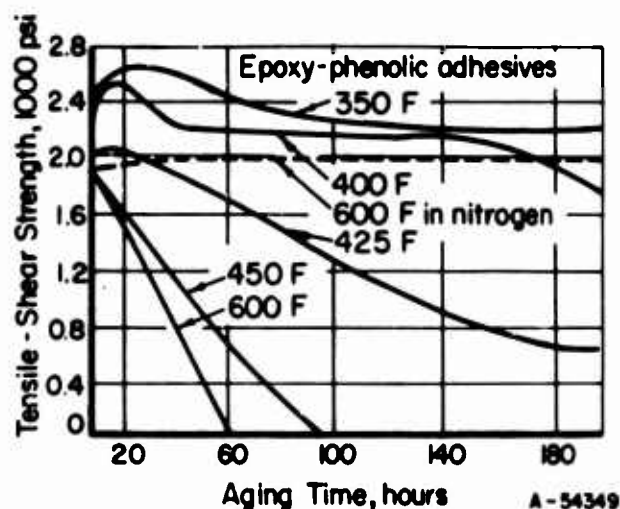
FIGURE 30. EFFECT OF TIME, TEMPERATURE, AND EXPOSURE
IN AIR OR IN NITROGEN ON TENSILE-SHEAR
STRENGTH OF JOINTS BONDED WITH AN EPOXY-
PHENOLIC ADHESIVE (REF. 69)

Adherends unspecified.

60

For adhesive-bonded joints intended for service in air, the degradation due to oxygen must be largely tolerated, although access of oxygen to the adhesive can be minimized by use of thin bond lines and clever joint design. The chemical nature of the metal ions diffusing into the adhesive from the adherends has also been found to be an important cause of deterioration of adhesives at elevated temperatures. Some metal ions accelerate the degradation reactions in the adhesive. Arsenic, a semimetal, in the form of pentoxide or sulfide, has been found to retard degradation and has been purposely added to some high-temperature adhesives.

Recent work by Flom, Speece, and Schmidt (Ref. 72) employing neutron activation analysis, electron paramagnetic resonance, thermochemiluminescence, infrared and mass spectrometry, and vapor phase chromatography, has shed new light on the detailed degradation mechanisms of epoxy, phenolic, and polybenzimidazole adhesives with aluminum and stainless steel adherends. The epoxy was found to degrade in two stages, the second of which is catalyzed by iron, but not by aluminum. Degradation of the phenolic adhesive was accelerated to some extent by aluminum and catastrophically by iron. Polybenzimidazole, though more stable than the other two adhesives, did degrade, and the degradation mechanism was different depending on whether the adhesive was in contact with aluminum or iron. Flom, et al, did not include the tensile-shear strength values for their specimens in their published report.

New High-Temperature Adhesives. The polybenzimidazoles (PBI) and polyimides (PI), are being investigated for service at temperatures above 350 F. Levine (Ref. 39) has coined the term "heteromatic" to describe the molecular structures of these adhesives, which have high proportions of aromatic and heterocyclic rings. The molecules tend to be spatially compact, with strong interatomic bonds that resist oxidative attack.

Data on tensile-shear strengths of 17-7 PH adherends bonded with PBI have been summarized by Litvak, Aponyi, and Tomashot (Ref. 73) for a range of temperatures and exposure times. Figure 31 shows the short-time strength of PBI between -423 and +1000 F for several adherends.

Figure 32 shows the effects of exposure times to 1000 hours at temperatures between 350 F and 700 F on the strength of PBI-bonded stainless steel and titanium adherends. Two stainless steels, 17-7 PH and PH 15-7 Mo, were used in the tests. Similar data are shown for a polyimide adhesive in Figure 33. Comparison between Figures 32 and 33 shows that the PI has better oxidation resistance than the PBI, though strengths are generally lower.

Reinhart and Hidde (Ref. 74) have reported the results of fatigue tests on PBI-bonded PH 15-7 Mo joints. The data are shown in Figure 34.

Freeman, et al, (Ref. 75) are conducting a developmental program on polyimide adhesives. The stainless steel adherends being used are AM-350. The investigators conclude that their best materials have life expectancies of about 1500 hours at 550 F and 40 hours at 700 F. A benzimidazole-imide copolymer has been shown to have superior properties with titanium adherends.

Cryogenic Temperatures. With the development of liquid-fueled rockets utilizing cryogenic propellants and the need to meet service conditions in space, programs have been undertaken to develop adhesive systems capable of retaining strength at extremely low temperatures such as -325 and -423 F, the boiling points of liquid nitrogen and hydrogen, respectively. Several adhesive evaluation studies have been made at -423 F (Refs. 76-80), and adhesives data have been included in PLASTEC Report 20 on cryogenic properties of plastics (Ref. 81).

The requirements for cryogenic adhesives reflected in low-temperature retention of joint strength include: thermal expansion coefficient approximately that of the adherend, resiliency as demonstrated by good peel strength at cryogenic temperatures, low curing shrinkage, high thermal conductivity, and an elastic

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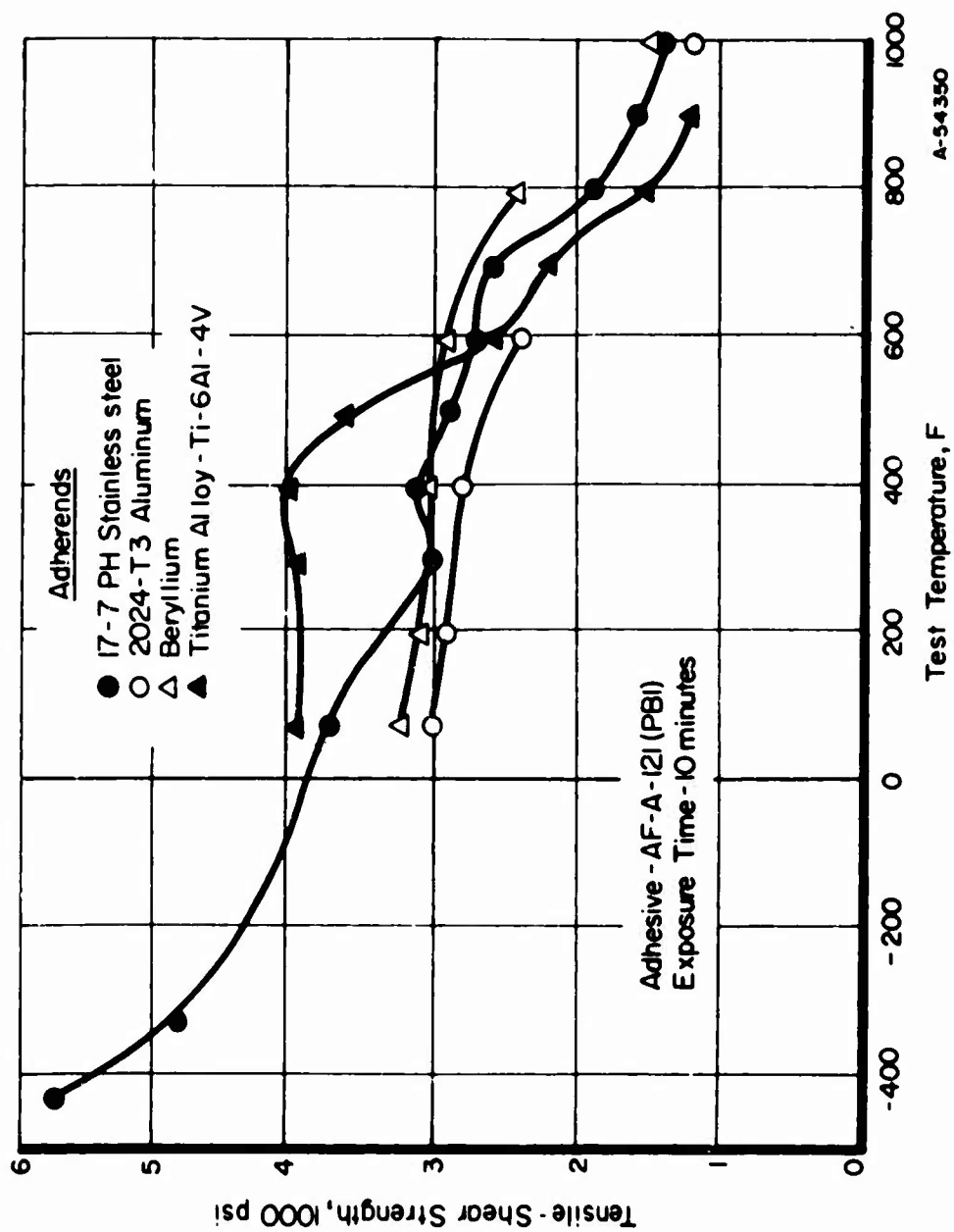
FIGURE 31. TENSILE-SHEAR STRENGTH OF PBI ADHESIVES ON VARIOUS SUBSTRATES (REF. 73)

63
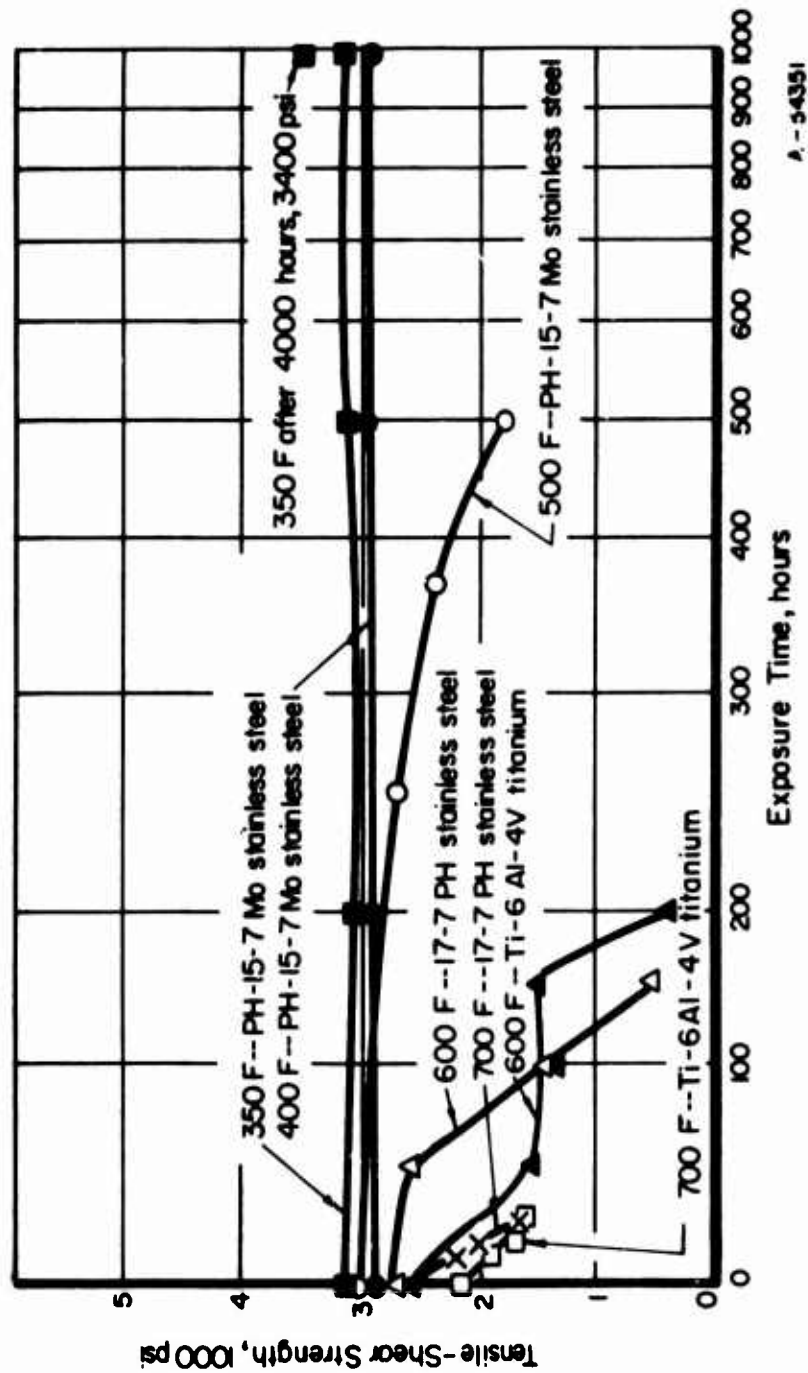
FIGURE 32. TENSILE-SHEAR STRENGTH OF PBI ADHESIVE ON VARIOUS SUBSTRATES (REF. 73)

64
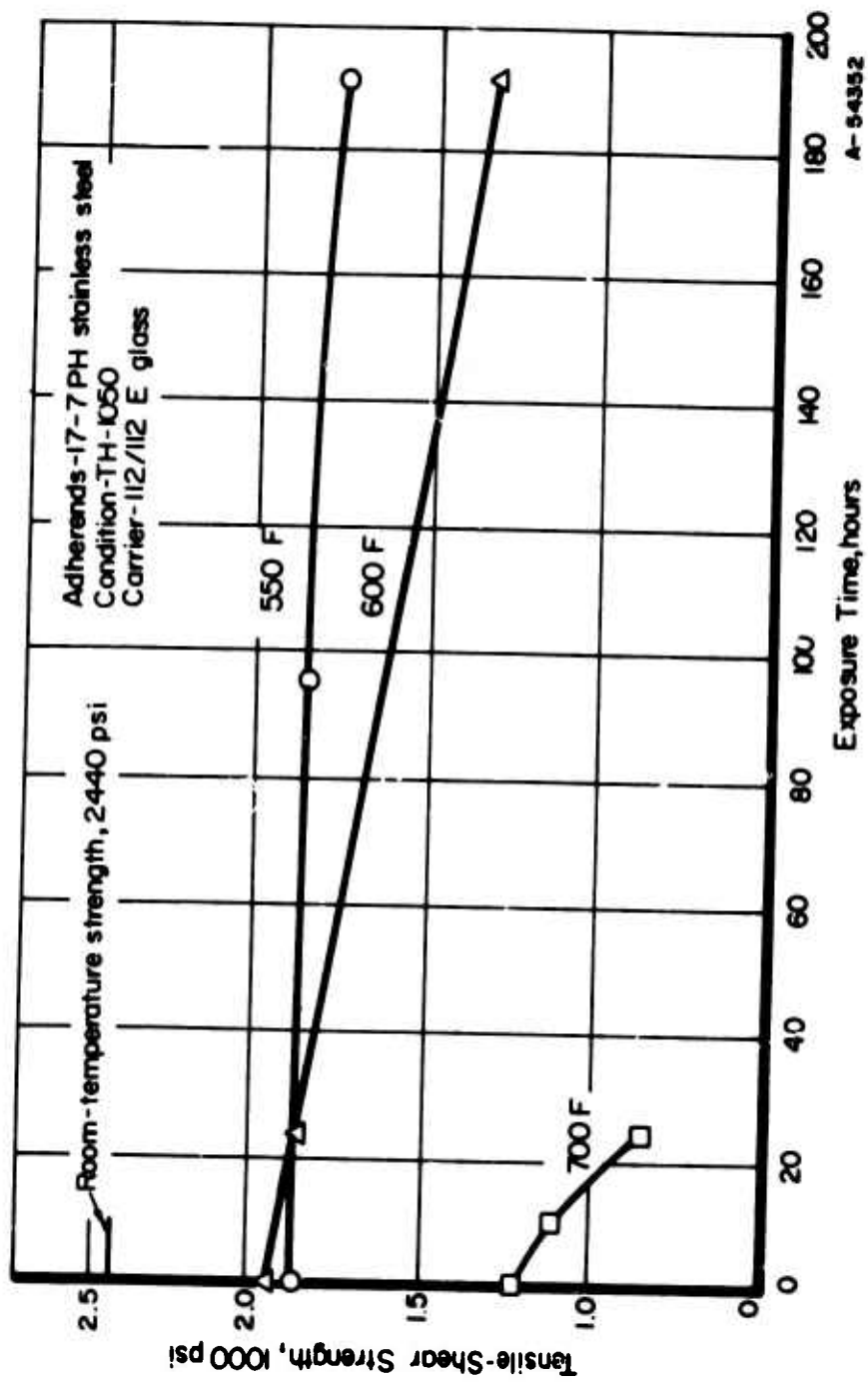
FIGURE 33. TENSILE-SHEAR STRENGTH VS. EXPOSURE OF POLYIMIDE ADHESIVE BONDED STAINLESS STEEL (REF. 73)

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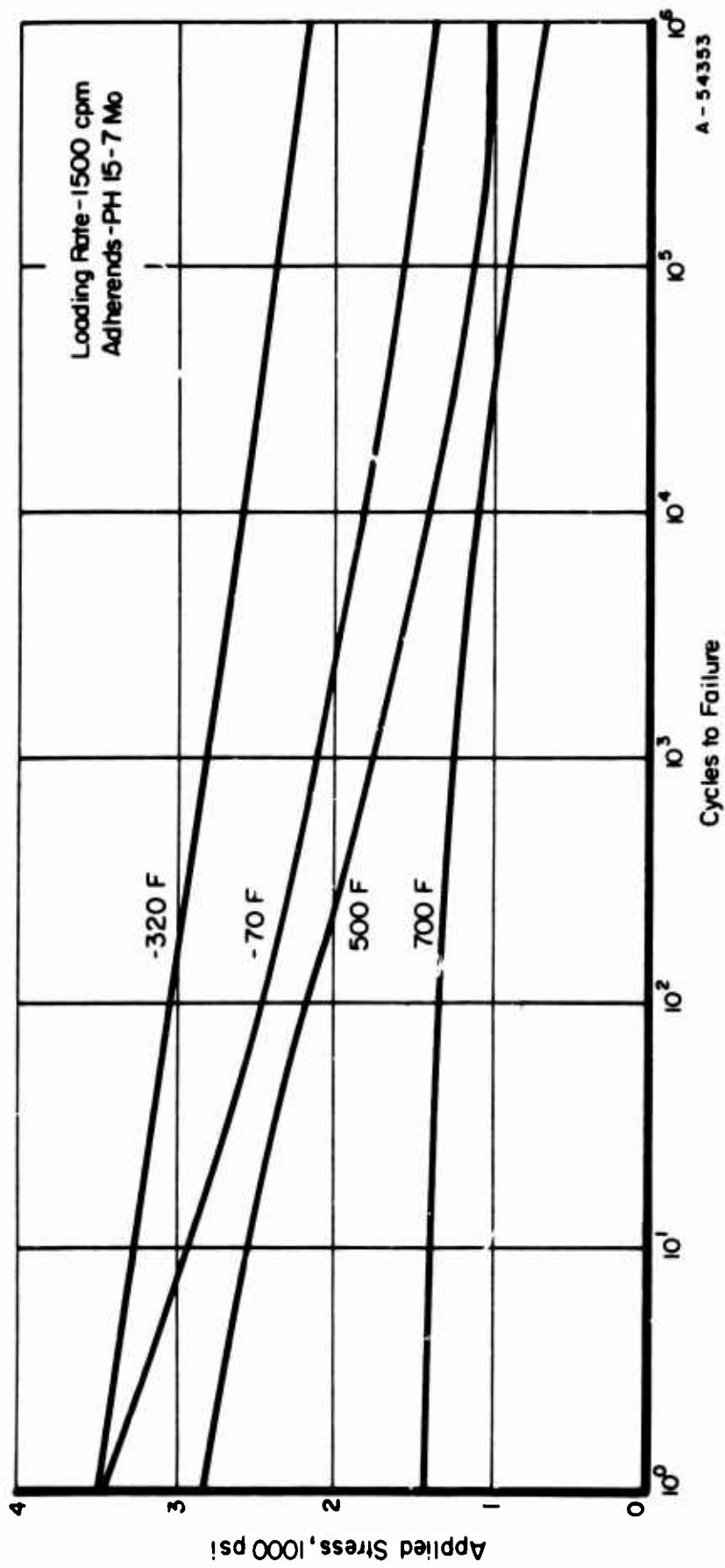
FIGURE 34. FATIGUE STRENGTH OF IMIDITE 850 JOINTS AT VARIOUS TEMPERATURES (REF. 74)

Loading rate - 1500 cpm
Adherends: PH 15-7 Mo.

66

modulus no greater than that of the adherend. Other desirable characteristics, some of which are of interest only in specific applications, include low specific gravity, long shelf life, short cure time, room temperature curing without pressure, sufficient flow to fill voids, good impact and vibration resistance, and freedom from reaction with liquid oxygen when mechanically shocked (LOX compatibility).

Kausen's survey (Ref. 69) includes adhesives for cryogenic temperature service. Figures 35 and 36, taken from his paper, summarize the tensile shear strengths of different adhesive types and some specified modified phenolic systems From Figure 22 it will be noted that polyurethane and epoxy-nylon adhesives have superior strengths up to around room temperature. As with high-temperature adhesives, however, these data should be applied to specific adherends with caution.

Figure 36 shows detailed data for specific adhesives of the modified phenolic class. It is interesting to note that the two rubber-phenolic blends had the highest and lowest shear strengths in the group, which emphasizes the fact that adhesives, even of the same type, differ widely in their properties.

British experiments (Ref. 82) have been conducted using stainless steel and titanium alloys bonded with epoxy adhesives in which tensile-shear specimens were repeatedly cycled between room temperature and various cryogenic temperatures. After ten complete cycles, the specimens were tested at room temperature. Temperature cycling caused little change in maximum strength but a noticeable increase in strength variation. The investigators noted an embrittling effect of the temperature cycling on the adhesives as evidenced by abrupt failures of cycled specimens during testing. Uncycled specimens pulled apart gradually.

Smith and Susman (Ref. 80) tested three of their developmental cryogenic adhesives using aluminum adherends, after twenty cycles between room temperature and -320 F. They, too, found no significant deterioration of tensile-shear strength following cycling.

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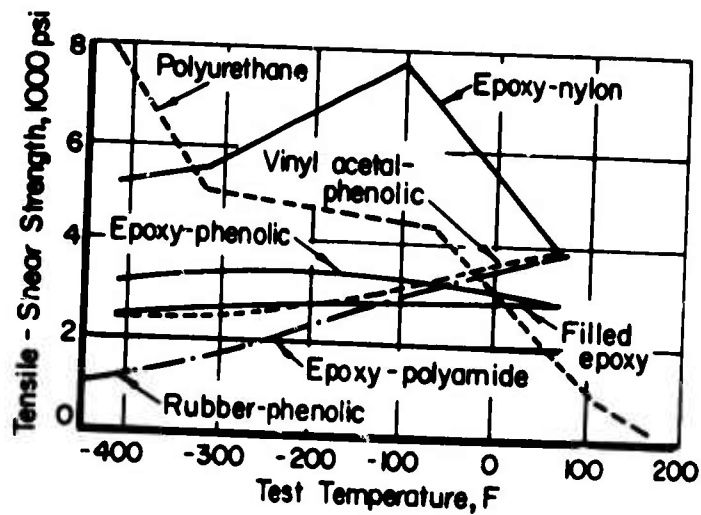
FIGURE 35. TENSILE-SHEAR STRENGTHS OF ADHESIVE SYSTEMS FOR CRYOGENIC SERVICE AS A FUNCTION OF TEMPERATURE (REF. 69)

Adherends unspecified.
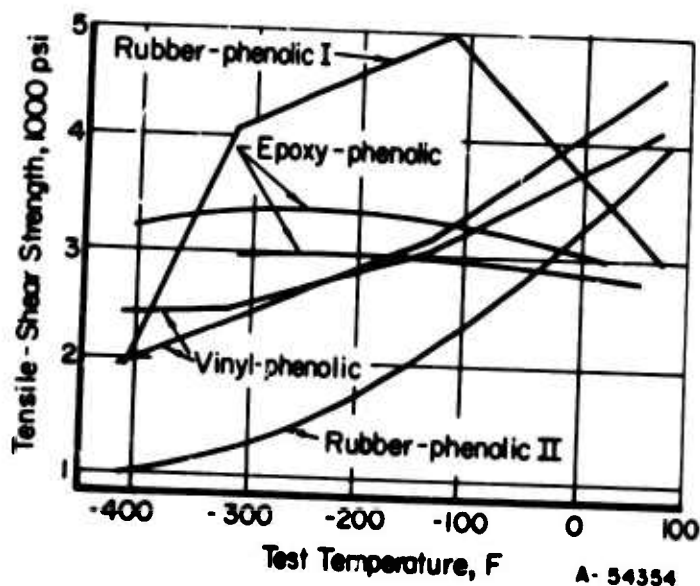
FIGURE 36. TENSILE-SHEAR STRENGTHS OF MODIFIED PHENOLIC ADHESIVES AT CRYOGENIC TEMPERATURES (REF. 69)

Adherends unspecified.

68

Polyurethanes are generally favored as adhesives for service at liquid hydrogen temperatures at the present time, despite their relatively poor properties above room temperature.

Radiation. Kircher and Bowman (Ref. 83) have summarized the known information on the effects of radiation on materials. Their book, though it does not deal specifically with adhesives, provides a timely and comprehensive view of the field of radiation damage. Several earlier reviews have been published that consider radiation effects on adhesives (Refs. 84-86). Two types of high-radiation environments are visualized as being of principal interest for possible applications of adhesive-bonded structures. These are the radiation fields in space and those in the vicinity of nuclear reactors. Radiation fields in space, so far as is known, consist principally of electrons, protons, and gamma radiation. Fields in and around reactors consist principally of neutrons, alpha particles, and gamma radiation.

Most organic materials, probably because of the low atomic numbers of their constituent atoms, are affected much the same by the different varieties of radiation. The damage mechanism consists of the transfer of large amounts of energy to electrons within the material by their interaction with the incident radiation, of whatever form. Organic materials, as a class, are sensitive to radiation dosage, and the differences in damage due to differences in type or intensity of radiation are secondary. Aromatic and heterocyclic (ring-containing) molecules are generally more radiation resistant than straight-chain polymers. Although in some cases there are constructive chemical reactions due to radiation bombardment, the common form of damage consists of bond rupture due to the high-energy electrons, with consequent loss in molecular weight and decreased mechanical strength and ductility. Organic materials as a class are more radiation sensitive than metals and ceramics. Radiation damage to an adhesive shows up first as a loss of peel strength.

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Radiation effects should be relatively independent of adherend except in those cases where the adherend itself becomes radioactive. The adherends, in fact, offer to the adhesive a degree of protection against soft radiation.

Figure 37, taken from Arlook and Harvey (Ref. 85) shows typical behavior of the tensile-shear strength of several adhesives, bonded to aluminum adherends, with increasing amounts of gamma radiation. Under room-temperature tensile-testing conditions, most of the adhesives showed continued loss of strength with increasing amounts of radiation. One adhesive showed a strength maximum, and another showed increasing strength over the entire range of dosage studied. For specimens tested at elevated temperatures following irradiation, the order of ranking of the adhesive strengths was somewhat different.

McCurdy and Rambosek (Ref. 86), using aluminum and stainless steel adherends bonded with a nitrile-phenolic adhesive, report that thick glue lines are less susceptible than thin glue lines to damage from gamma radiation as measured by tec-peel strength (Table IV). The same investigators report the results of tests made on honeycomb panels using composite film adhesives. In these composite adhesives, which are fairly widely used for honeycomb fabrication, a glass-cloth carrier is coated on the face-sheet side with a flexible adhesive for peel strength and is coated on the core side with a more rigid adhesive that has better filleting characteristics. Loss of peel strength following irradiation was found to be severe, adhesion failure occurring on the core side.

The amounts of radiation required to cause serious deterioration of adhesive bonds appear to be such that adhesive bonding can be considered for use in space for missions lasting at least of the order of months. The new heterocyclic adhesives, such as the polybenzimidazoles, should be less radiation-sensitive than types heretofore available. However, adhesives that can withstand the intense radiation found in the immediate vicinity of nuclear reactors are not presently available.

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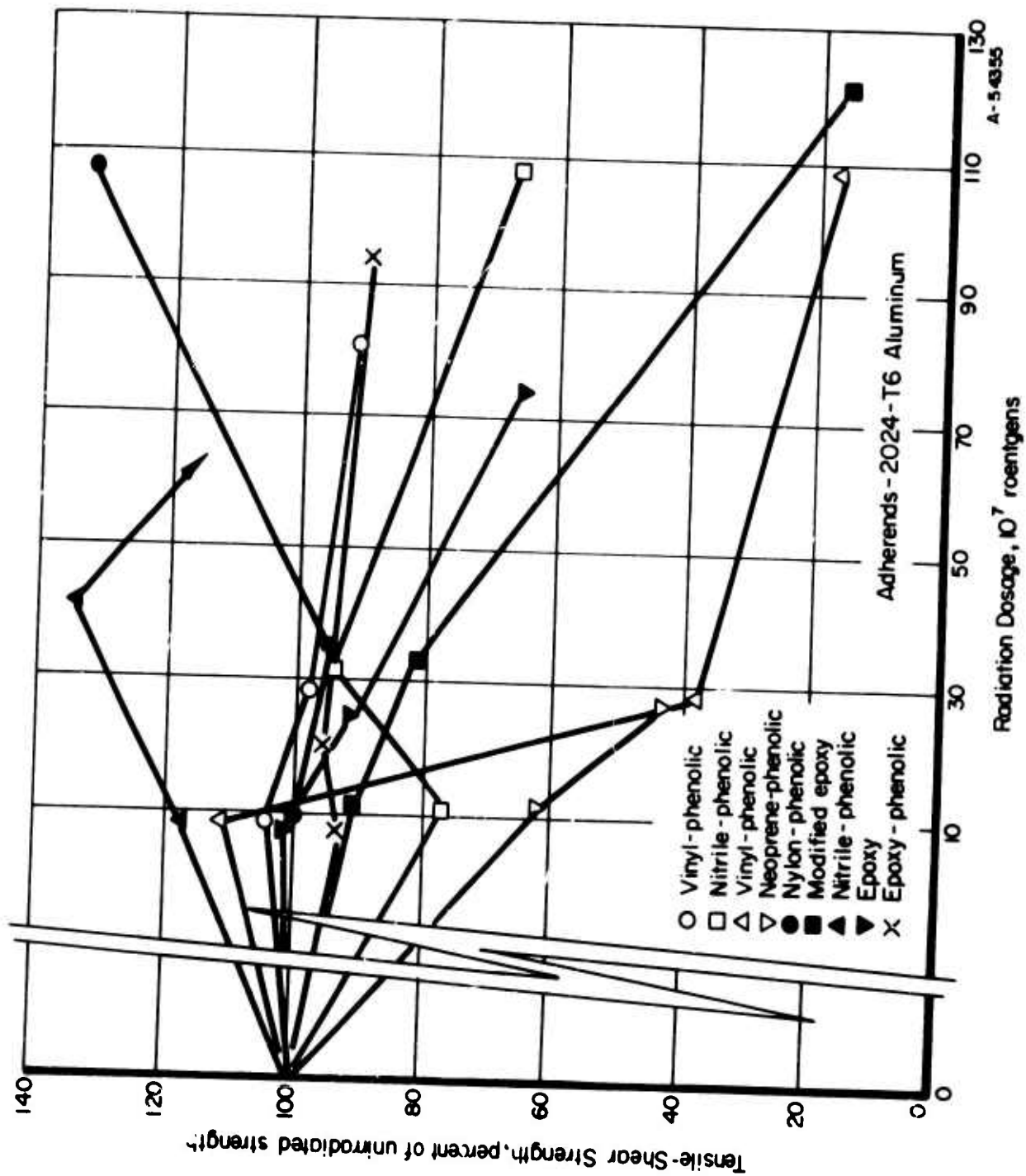
FIGURE 37. TENSILE-SHEAR STRENGTH VERSUS RADIATION DOSAGE (REF. 85)

Specimens tested at room temperature.

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TABLE IV. EFFECT OF GLUE-LINE THICKNESS ON TEE-PEEL
STRENGTH OF A NITRILE-PHENOLIC ADHESIVE
WITH RADIATION EXPOSURES (REF. 86)--
STAINLESS STEEL ADHERENDS

Glue-Line Thickness, mils	Tee-Peel Strength, in-lb/in., At Indicated Dosage, megarads				
	None	100	300	600	900
1.2	10	7	5	3.5	2.5
3.7	14	9	7	4	2.5
10.0	30	20	9	3.7	3.5
16.1	19	14	6	4.5	3.5

Combined Variables. Relatively little is known concerning the influence
on adhesive-bonded joint strength of the interaction effects between simultan-
eously applied environmental variables. Adhesives are commonly tested by exposing
joints to these variables singly. Sharpe (Ref. 87) has recently reported the
existence of a hitherto-unsuspected interaction between humidity and mechanical
stress. This effect consists of a substantial and progressively increasing loss
of strength with time, an example of which is shown in Figure 38. The shapes of
the curves are similar to those of stress-rupture curves for metals. Although
the curves presented are for a cyclic environment (Figure 39), the effect also
occurs under static humidity-stress conditions. Sharpe did not reveal the identi-
ties of the adhesives tested, but stated that he found significant strength losses
in all types of adhesives. The effect was shown to occur with 2024-T3 aluminum
and Type 302 stainless steel adherends.* Relative strength loss for the two ad-

* A simple surface preparation was used for the stainless steel, with "reliable,
  excellent" results. It consisted of vapor degreasing, followed by 15 minutes
  at room temperature in a 12 weight percent HC solution, rinsing in distilled
  water, and drying with oil-free compressed air.

72
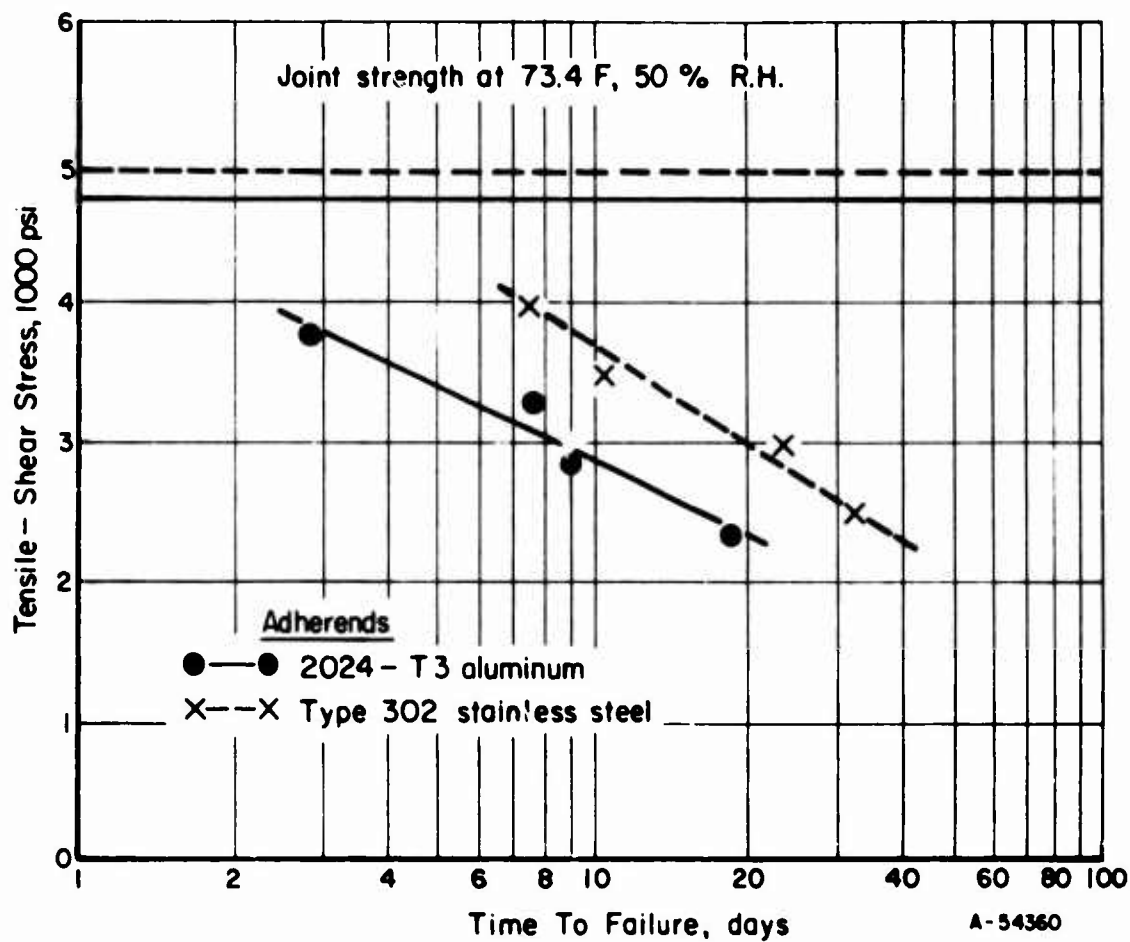
FIGURE 38.   TIME TO FAILURE VERSUS STRESS FOR ADHESIVE
Z IN ENVIRONMENT C (REF. 87)

73
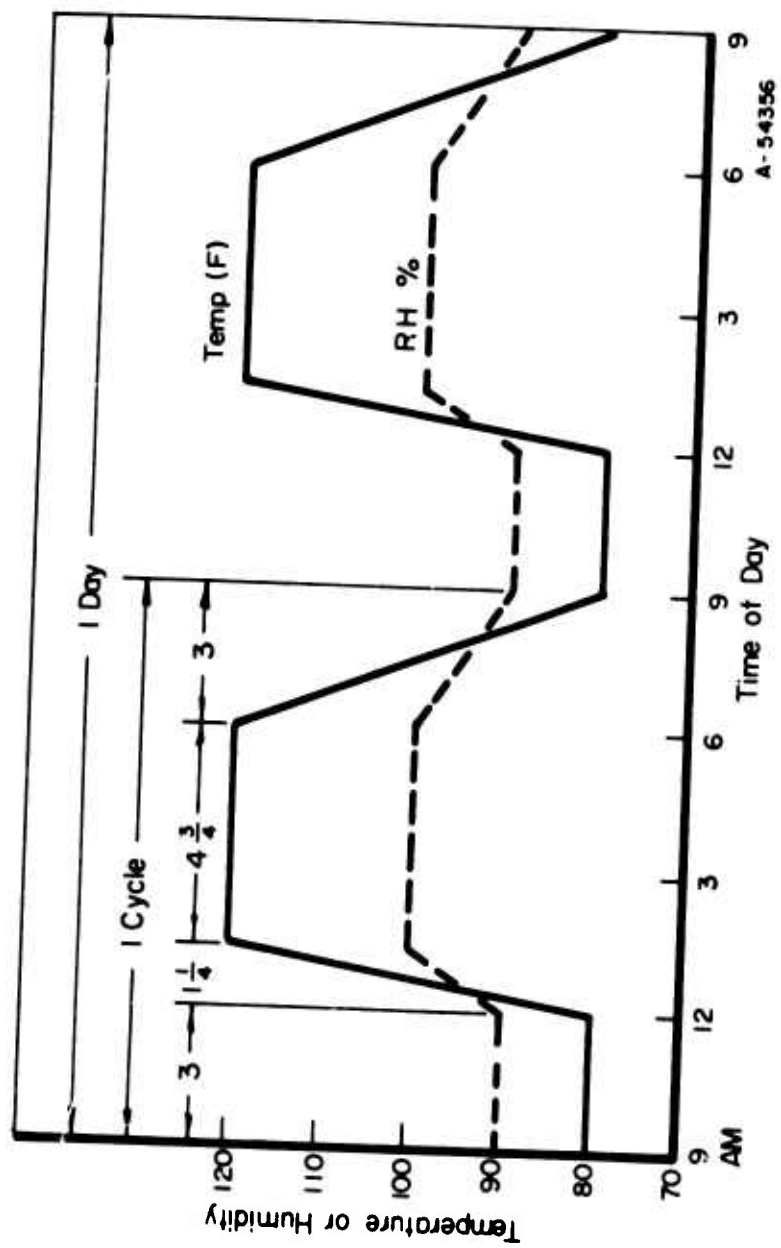
FIGURE 39. CYCLIC TEMPERATURE-HUMIDITY TEST ENVIRONMENT
(ENVIRONMENT C) (REF. 87)

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herends differed for different adhesives. Ruptures occurred with no prior deforma-
tion of the adhesives. The failure mechanism is not yet understood.

APPLYING THE ADHESIVE

The manner in which adhesives are applied to adherend surfaces will depend
upon the form of the adhesive and the production rates desired. Thick liquid
adhesives can be applied by roller coating, brushing, troweling, or dip coating.
Thinner liquids can be brushed on, flow coated, or sprayed. Dip coating is useful
only for joint geometries that do not result in much adhesive loss or for parts
that can be wiped to remove adhesive from areas of the part where it is not desired.
Flow, or curtain, coating is a high-production process widely used in the plywood
industry. Flat parts are passed under a flowing curtain of adhesive. Tapes and
films can be conveniently hand applied if the adherend is first laid out on a
heated table. Alternatively, the adherend may be laid on an unheated table and a
tacking iron used in spots to cause sufficient adhesion of the film to the adherend
to hold the adhesive in place. Film adhesives are popular in aerospace structural
bonding because they are neat and clean to apply. Adhesives in powder or stick
forms do not appear to be as widely used as liquids, pastes, and films in this
country for metal-to-metal adhesive bonding. Powders, when used, have been applied
by sprinkling over the adherend or by immersing the heated adherend in a fluidized
bed of the powder adhesive.

When two-part liquid adhesives are used, they must be adequately mixed and
applied with minimum delay after mixing, since their working lives are limited.
Mixing and dispensing equipment for two-part adhesives is designed for accurate
metering and proportioning of the components of the adhesives. The actual mixing
is usually done in the dispensing nozzle just before the adhesive emerges. The
apparatus, and especially the nozzle, is designed for easy cleaning.

Most aerospace adhesive bonding applications involving two-part adhesives
are hand lay-up operations involving small quantities of adhesive. When adhesive

quantities are sufficiently large that hand mixing is too slow, use of metering
and dispensing equipment should be considered.

TOOLING AND FIXTURING--JOINT ASSEMBLY

When bonding with adhesives that release water, solvents, or other volatile
substances during curing, it is often necessary to clamp the adherends in proper
relation to each other with pressures up to several hundred pounds per square
inch. With "100 percent solids" adhesives, such as the epoxies, such curing
pressures are not necessary except in critical work where clamping will be used
to control glue-line thickness and alignment. Manufacturer's instructions for
the specific adhesive should be followed. In some cases, parts can be made
self-aligning and self-clamping by appropriate design.

Methods of applying pressure during curing will depend upon the size and
shape of the part, the magnitude of the pressure to be applied, and the quantity
to be produced. There are several basic methods in use. The simplest method
is to make the adherends self-clamping. Another method is to combine adhesive
bonding with another fastening method such as riveting. Dead-weight loading can
also be used for parts having simple shapes.

For parts having more complex shapes, the vacuum-bag technique can be used
as shown in Figure 40a. The vacuum-bag method is limited to pressures below
14 psi, however. Where higher pressures are necessary, the pressure-shell method
shown used with a heated mold in Figure 40b can be used. With the pressure-shell
method, pressure is limited only by the mechanical design of the confining parts.
It could be used equally well with oven curing as shown in Figure 40a, and, in
the same way, the vacuum-bag method could be used with a heated mold.

The autoclave method shown in Figure 40c is more elaborate. The
part must be sealed into a flexible-blanket assembly vented to atmosphere
so that a differential pressure across the bond can be applied. A hot-inert-gas
atmosphere under forced circulation is used in the autoclave. Use of a sheet-

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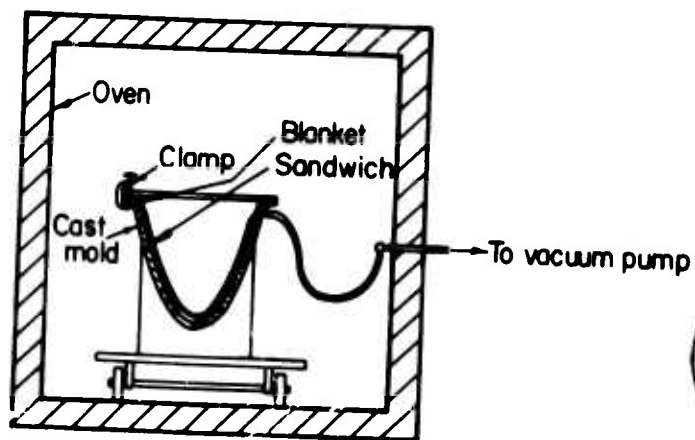
a. Vacuum - Bag Curing
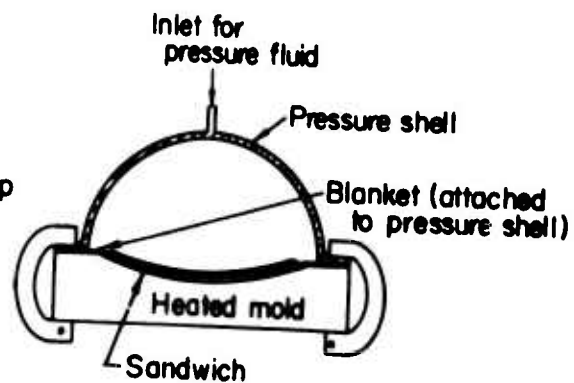
b. Pressure-Shell Curing
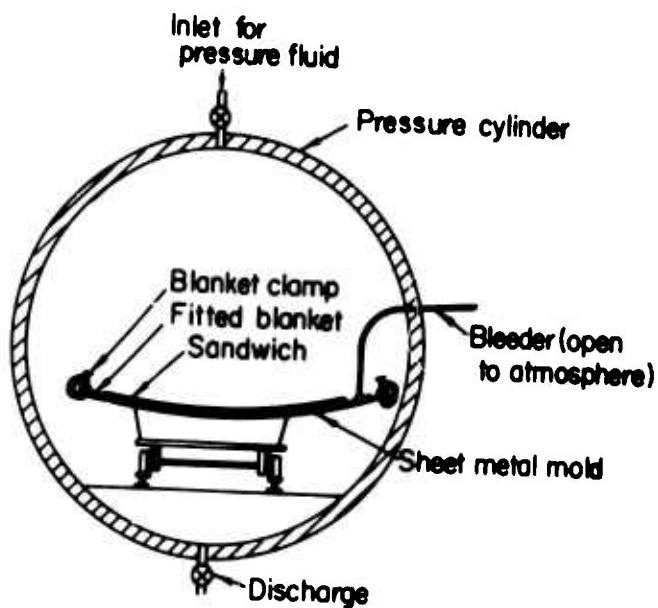
c. Autoclave Curing
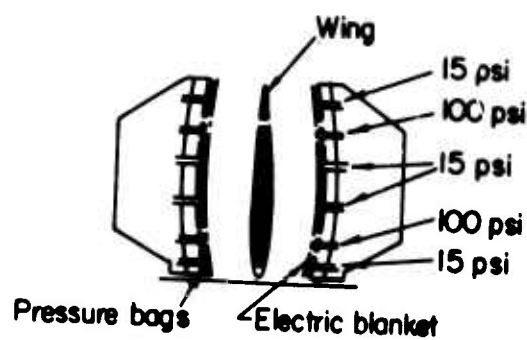
d. Press Curing

A-54357

FIGURE 40. METHODS FOR CURING ADHESIVE-BONDED ASSEMBLIES (REF. 43)

metal mold is shown with the autoclave. This type of mold can be used if it is not essential to maintain the maximum degree of smoothness on one side of the bonded assembly. However, for such applications as aircraft skins, in which the exterior surface must meet stringent aerodynamic requirements, a rigid mold must be used for the exterior, all tolerance mismatches being taken up on the back, or interior, side of the panel. For those situations where both surfaces of a bonded assembly must meet smoothness and shape requirements, tolerances of parts to be bonded must be held very closely, and heated presses such as the one shown in Figure 40d must be used.

CURING

Usually, but not always, the adhesive manufacturer's recommended curing conditions will result in bonds of optimum quality in a given application. Where maximum properties are important, such as for aircraft skin panels, development work by airframe manufacturers has resulted in complex curing cycles in which heating rates are controlled, and temperatures and pressures are varied during the cure in a precise manner.

Adhesive systems of the film and liquid types are available that cure at room temperature. Precautions to be observed with this type of adhesive are: (1) be certain that the working life has not been exceeded before use, and (2) keep the volume of adhesive small. Considerable heat is often generated during curing.

Novel Curing Techniques. Curing can sometimes be accomplished in ways which take advantage of heating done for other reasons. In some automotive applications, for example, the adhesive is cured by the heat applied to dry the body enamel.

Radio-frequency dielectric heating is sometimes used to cure adhesive bonds in which the adherends are insulators, such as wood or plastics. Smith and Susman

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(Ref. 88) have reported results of the application of direct and alternating electric potential across a metal-to-metal bond. The direct voltage is to be avoided, since it results in electrolysis of the adhesive, but slight increase over room temperature-cured strengths resulted from a 700-volt alternating potential (frequency not specified) with an epoxy-polyamide adhesive. Hagberg (Ref. 54) has achieved very rapid cures with metal-to-metal bonds with r-f energy directly applied through adherend contacts.

North American Aviation (Ref. 89) has developed a film adhesive containing an array of fine, high-resistance wires. Current is passed through the wires for a sufficient time to accomplish the cure. When a wing flap cured in this manner was tested in peel, failure occurred in the rivets used to attach the flap to the testing frame at 7.5 times design load. The adhesive-containing resistance wires is commercially available.

Bandaruk (Ref. 90) has reported on theuse of internal electrical resistance heating elements of graphite fabric. Sandwich panels were bonded using an epoxy adhesive, and tensile-shear specimens were prepared with a hot-melt adhesive.

Another novel approach to adhesive curing consists of using an exothermic-adhesive-reaction mixture (Ref. 91). The mixture is placed between the surfaces to be bonded, and they are then clamped in contact. The parts are then heated to the ignition temperature of the exo-reactant mixture, whereupon the reaction takes place, and a cured adhesive bond results. It is apparent that the short time at temperature limits the adhesive composition to one which will cure rapidly.

CLEANING THE CURED JOINT

Very little cleaning of the cured organic adhesive-bonded joint is usually necessary, and most often none is performed. Any adhesive extruded from the bond line can be removed by scraping or single-point machining, if its removal is required.

TESTING AND INSPECTION

The importance of testing for adhesive acceptance, process control, and outgoing quality assurance cannot be overstressed. Lot-to-lot variation in adhesives is sometimes significant for critical applications. Adhesives and primers already in-plant must be checked before and during use to be certain that they have not deteriorated with age or improper storage conditions. The adherend surface preparation process must be continually monitored, and the curing process controls must be in calibration. Finally, the bonded parts must be inspected to assure quality. Successful manufacturers of high-integrity adhesive-bonded structures invariably maintain effective testing programs. Some have gone to great lengths to establish their own tests. The literature on adhesive-bond testing is extensive (Refs. 3, 63-65, 92-98, for example), and only a few salient features will be mentioned here.

Adhesive Evaluation. General Dynamics (Ref. 68) uses the tensile-shear test for incoming batches of adhesive, a peel test for day-to-day checking of adhesive quality and adherent cleaning efficiency, a beam-compression test if the adhesive is to be used in honeycomb bonding, and a flow or gel time test to measure ability of the adhesive to flow and wet the adherend surface. In the case of low-flow adhesives, measurement of compressibility is substituted for the flow test. Filleting strength of adhesives intended for bonding honeycomb is measured by a variant of the pi-tension test in which a circular skin sample is bonded to a core and the skin is then pulled in tension.

Tooling Evaluation. Before bonding tools and fixtures are placed in production, they must be proved by making destructive tests on parts bonded with them. Process equipment and instrumentation must be periodically checked to insure satisfactory operation. On-the-spot inspection during adhesive bonding is necessary to enable adjustment of processing equipment with a minimum scrap loss of product.

Destructive Testing. It is desirable to hold to a minimum any destructive testing that renders the bonded parts unsuitable for service. One way this objective has been met is through the use of small detachable test coupons. Planning for this type of testing must be done at the time the tooling is designed. The specific tests performed will depend upon the nature of the bonded parts and their intended service. Use of test coupons does not entirely eliminate the need for some destructive testing of the parts themselves. Use of the Portashear test has already been mentioned.

Nondestructive Testing. The test techniques most widely used are adaptations of ultrasonic test methods developed for metals, and may be carried out with the parts immersed in water or dry with only a fluid-coupled transducer. Several types of sonic test equipment are available from United States and foreign manufacturers.

At the very least, sonic bond-testing equipment can detect unbonded regions in adhesive joints. The Fokker Bond Tester can locate such flaws on the remote side of a honeycomb panel. However, if detection of unbonded regions is the only information desired, they can also be located by a skilled inspector using a coin or a special light hammer to tap the part. Ultrasonic testers are capable of giving additional information concerning adhesive-bonded joints. Correlations have been made between Fokker Bond Tester reading and tensile-shear or face sheet bond strength, so that as-bonded strengths can be predicted (Refs. 99,100). Several aerospace manufacturers have worked out these correlations for their particular bonding systems, and they are presently being used in quality control.

An attempt has been made to carry the use of the sonic tester one step further, viz., to detect in-service bond-strength deterioration (Ref. 101). This attempt was not successful. Tester readings did not give consistent correlation with losses in bond strength following exposure to salt spray, boiling water, high

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temperature, vacuum, gaseous and liquid fluorine. and FLOX (30 percent F_2 and 70 percent O_2).

Sonic/ultrasonic emission, consisting of the detection and amplification of the noise generated within a specimen with increasing load, has been applied to adhesive-bonded joints (Ref. 102). It was found that an easily detectable increase in the noise at frequencies above 16 kc occurred as the applied stress exceed 70 to 80 percent of the fracture stress. Presumably this change in the character of the sound emission was associated with local yielding or micro-cracking of the adhesive. If the specimen is unloaded without exceeding this microyield point more than a small amount, Schmitz and Frank believe that the structure will still be serviceable. The method should be useful in proof test-ing of complex parts and pressure vessels. If was not established whether the 16 kc threshold is a function of specimen size or shape. The technique was not successful with a highly flexible polyurethane adhesive.

Among other methods that require the mechanical stressing of the part being tested are the use of brittle or birefringent (Ref. 103) coatings. These tech-niques, although successful in detecting unbonded honeycomb face sheet regions, give no indication of bond strength. The birefringent coating can be used to determine the residual stresses in face sheets following pressure testing. Unlike the sonic/ultrasonic emission technique, both of these methods are sensitive to face sheet thickness.

Thermal techniques have been used for examining honeycomb core-to-face sheet bonds, with much the same limitations as the brittle and birefringent coatings. The methods are based on differing cooling rates of the face sheet in bonded and unbonded areas. One system designed for checking the bond between solid-rocket motor fuel and the motor case liner used a traveling radiant heat source followed by an infrared pickup of the thermopile type (Ref. 104). A continuous chart record of the scan was kept, and unbonded regions appeared as hot spots. The method de-

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tected 1/2-inch-wide unbonded regions, but has the disadvantage that considerable time may be necessary to scan a large part, a disadvantage it shares with sonic flaw testing.

Other thermal techniques have employed waxes or organic compounds that melt or change color with temperature. The compound is applied to the entire face sheet, following which the specimen is heated. Unbonded regions appear as hot spots because of their relative inability to conduct heat into the core. Although the entire specimen can be examined at the same time, the effect for which one is looking is transient, and there are problems in heating the specimen uniformly. The most recently reported investigation of a method of this type (Ref. 105) made use of "liquid crystals" that show a very sharp and reproducible color change at a desired temperature.

Although some X-ray examination of adhesive-bonded parts has been done, nondestructive tests based on introduction of sonic waves give more information and are most widely used. Unlike the case of brazed honeycomb, where X-ray is a major inspection tool, adhesive bonds are transparent to X-rays of the energies necessary to penetrate metal cores and face sheets.

Schmitz and Frank (op. cit.) have studied the electrical properties of the bond line without obtaining any correlation with strength. They were unable to obtain repeatable values of d-c resistance, loss tangent, and dielectric constant, and concluded that these are not promising nondestructive test methods for adhesive-bonded joints.

The same investigators devoted considerable effort to possible methods for applying mechanical stress to panels for nondestructive testing. This information is noted here because of its possible value to others concerned with such testing, but is beyond the scope of this report.

BONDING STAINLESS STEELS WITH INORGANIC ADHESIVES

As part of a continuing search for adhesive bonding processes having improved elevated-temperature service capability, the Air Force and the Navy sponsored work on inorganic (ceramic) adhesive development with several organizations during the years between 1954 and 1962. Adherends used were principally 17-7 PH, although some work was done using PH 15-7 Mo, AM 350, Inconel X, and René 41.

While the results of this program fell short of desired objectives in some respects, particularly in the failure to achieve satisfactory mechanical shock resistance, significant results were obtained that may still be useful. Remarkable slow bend joint ductilities and service temperatures (800-1000 F) considerably in excess of those of the organic adhesives available at the time were achieved with stainless steel adherends. Somewhat higher service temperatures were achieved with superalloy adherends.

The improved service temperatures over those of organic adhesives are the only apparent advantage of the inorganic adhesives. With the development of polybenzi-midazole and polyimide adhesives having service temperatures in the 600-700 F range, the temperature advantage of the inorganics has lessened and will probably lessen further as improvement of organic adhesive systems continues.

Ceramic adhesive bonding must compete with brazing as a fabrication process. The ceramic adhesives are potentially less expensive than brazing alloys, do not require vacuum or protective atmospheres during firing, and require less precise tolerances than brazing. The ceramic adhesives are not likely to attack or embrittle the adherends, sometimes a difficulty with brazing. Because of the relative inertness of the adhesives, joints can be refired if necessary. Firing temperatures and times do not have to be controlled as precisely as with brazing for many joints.

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The disadvantages of ceramic adhesive joints with respect to brazed joints are considerable, however. Among these disadvantages is that the adhesives weigh at least twice as much per unit area of joint. In complex aerospace structures containing considerable bonded area, such as honeycomb panels, the weight penalty associated with the inorganic adhesives becomes appreciable. Weight, plus the poor resistance of ceramic adhesive joints to shock and impact loading and their lower unit mechanical strengths compared with brazing alloys have resulted in the selection of brazing in preference to ceramic adhesive bonding for production applications.

SURFACE PREPARATION OF ADHERENDS

Procedures for surface treatment of stainless steel adherends prior to bonding with inorganic adhesives have varied in complexity among the different investigators. Most have treated the surface preparation as incidental to the investigation and have not reported their procedure in detail. It is probably true that surface treatment is not as critical as for organic adhesive bonding because of the higher firing temperatures involved and the (assumed) ability of the ceramic to absorb the amounts of contaminant metal ions likely to be present without affecting the adhesive materially. Nevertheless, the one group that did study the adherend preparation process in detail found that bond strength was significantly decreased if any step in their procedure was omitted.

The simplest procedure used for surface preparation, used for 17-7 PH, was at the University of Illinois (Ref. 106), and consisted of a sandblasting treatment.

Investigators at Boeing/Wichita (Ref. 107) also tried sand- and shot-blasting, but found both processes unsuitable because they distorted the thin-gage sheet being used in the fabrication of honeycomb panels. Boeing then settled on a treatment consisting of a vapor degrease followed by an alkaline cleaner. Some work was also done using a hydrofluoric-nitric acid etch.

Bayer, Johnson, and Patterson (Ref. 108) report in detail the development of the surface treatment adopted at Aeronca for use on 17-7 PH, AM-350, PH 15-7 Mo, and Inconel X nickel-base alloy in the honeycomb panel application. Panels produced consisted of 0.032-inch 17-7 PH facing sheets, 0.500-inch 17-7 PH and 0.002-inch foil, 1/4-inch cell core bonded with ACA 100-1 adhesive. The process consisted of the following steps:

Surface Preparation of Facing Sheets

NOTE: Handle all parts with clean white cotton gloves.

A. Cut sheets to size.

B. Vapor degrease facing sheets using best practice.

C. Lay skins on the firing rack. The skins should be separated from each other. Any support should touch the nonbonding side of the skin.

D. Place in furnace at 1000 F (1200 F for Inconel X) for 30 minutes to heat scale the sheet.

E. Remove from furnace and air cool.

F. Place vertically in an acid bath of 20% by volume of 63% nitric acid and 4% by volume of 70% hydrofluoric acid for 5 minutes at 150-160 F. If all of the scale is not removed, return to the etch. Excess etch time should be held to the absolute minimum. At no time should the total immersion time in the etch exceed 7 minutes.

G. Cold water rinse for 5 minutes. Wipe off smut with soft, clean cloth. Rinse and return to complete rinse for 5 additional minutes.

H. Place the skin in a neutralizer water solution of 0.16 oz/gal of borax and 0.48 oz/gal soda ash at 125-130 F for 30 minutes.

I. Cold water rinse for 10 minutes.

J. Air dry vertically, with forced ventilation.

Surface Preparation of Core

A. Cut core to size.

B. Vapor degrease using the best practice. NOTE: Core should be in horizontal position.

C. Core position (horizontal or vertical) is optional during the heat scaling.

D. Place in furnace at 1000 F for 30 minutes.

E. Remove from furnace and air cool.

F. Place the core horizontally in the acid etch bath referred to above for approximately 3 minutes. If the etching and heat scale removal are not completed, the etching may be continued in 30-second increments. Excess etch time should be held to the absolute minimum. At no time should the total immersion time exceed 5 minutes.

G. Rinse in cold water for 10 minutes. The core should be agitated to aid removal of the heat scale.

H. Place in the 0.16 oz/gal borax, 0.48 oz/gal soda ash solution at 125-130 F for 30 minutes. Agitate core occasionally to assure neutralization of all acid in capillaries.

I. Cold water rinse for ten minutes.

J. Air dry in the horizontal position with forced ventilation.

ADHESIVE SELECTION

An inorganic adhesive for bonding stainless steels would probably be selected and compounded by duplicating the best recipe and joint preparation procedure from the research investigation reports mentioned earlier. For one to consider inorganic adhesive bonding, service temperature would have to be between about 500 and 1000 F. At lower temperatures, an organic adhesive would probably be specified, and for higher temperatures, a different alloy would probably be used.

The ceramic adhesives for which information is available are compositions of borosilicate glasses plus metal or crystalline oxide phases. The compositions developed were arrived at after due consideration for wetting of the adherend, matching the adherend thermal expansion coefficient and elastic modulus as closely as possible, and attainment of good mechanical strength. Unless one is prepared to undertake an extension of the research done to date, the choice of adhesives is limited. A specific adhesive recipe and bonding procedure will be discussed in subsequent sections.

PREPARATION OF INORGANIC ADHESIVES

Once the desired adhesive and composition has been specified based on the required thermal expansion coefficient, softening point, and elastic modulus, the raw material recipe can be calculated. The raw materials will consist of such compounds as the oxides, carbonates, nitrates, silicates, etc., of the constituent metals. Raw materials should be of a high degree of purity, since presence of minor quantities of undesired metals can change the physical and mechanical properties of the finished ceramic adhesive.

The raw material charge is placed in a crucible and raised to the smelting temperature. Care should be taken in the selection of the crucible material to avoid crucible-charge reactions. A fireclay crucible has proved satisfactory for the compositions used in past ceramic adhesive work on stainless steels. The smelting furnace can be gas-fired, and the smelting is done in air.

After smelting, the molten charge is poured into a water tank. The rapid cooling rate causes the shattering of the material into a powder, or frit. The frit is dried, following which it is sized by passing through a set of graded sieves. A wet or dry grinding operation may be interposed between fritting and sizing.

Both the average size and the distribution of particle sizes will influence the subsequent behavior of the ceramic.

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The sized frit, plus additives, is charged to a ball mill or a blender for mixing and further sizing. The additives typically will consist of metal powders intended to increase strength and ductility, suspending agents such as ammonium molybdate to control slip properties, possibly some organic binder, and water. Product from this operation, having the form of a slurry, or slip, is ready for application to the adherends at this point.

The technology of ceramic slips is complex. The natural settling tendency of the insoluble ceramic and metal particles is offset by the fact that part or all of the particles are in the colloidal size range and thus will tend to remain in suspension. As is common with colloidal suspensions, however, there may be a tendency for the slip to gel, or "set up" with time. The metallic and dielectric particles themselves would also tend to agglomerate and settle out rapidly if it were not for their being electrically charged, all with the same sign. Careful control of the pH of the slip is necessary to maintain the proper suspension and flow characteristics. The reader should consult up-to-date textbooks on ceramic science and technology for detailed discussions of the rheology of slips.

The detailed procedure used at Aeronca for preparing the ACA 100-1 adhesive is as follows:

Preparing the Adhesive

A. Raw Materials, Frit ACA 100-1	%	Grams/ 2000-batch
400 Mesh Silica, Chicago Vitreous	24.5	490
Sodium Nitrate, Coarse Granular, Tech.	8.8	176
Boric Acid, Chicago Vitreous	65.2	1304
Ferric Oxide, J. T. Baker	1.5	30

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B. Calculated ACA 100-1 Frit Oxide Composition

SiO_2	37.2%
Na_2O	4.9%
B_2O_3	5ɔ.9%
Fe_2O_3	2.0%

C. Method of Manufacturing Frit

Basic laboratory size batch - 2000 grams of raw materials.

1. Heat the smelter and smelting crucible slowly, during a 1-hour period, to approximately 2400 F.

2. Add approximately 1000 grams of the well-mixed raw materials.

3. Heat at 2400 F for approximately 20 minutes until most of the frothing has stopped and volume reduction is obvious.

4. Add the rest of the raw materials.

5. Heat at 2400-2500 F for 60 to 90 minutes until all frothing has stopped and a pulled thread of the glass contains no bubbles.

6. Quench the molten glass in a 3-gallon bucket of cold water. Slow pouring is necessary to produce the smallest possible frit.

7. Remove the excess water by draining. Dry the frit thoroughly in an oven at 250 F for a minimum of 3 hours.

D. Milling of the Frits and Preparation of the Slip

1. Fill a dry 3-quart capacity ball mill to 40% of its capacity with 50% 1/2" porcelain balls.

2. Add the frit to the 3/4 level of the mill.

3. Mill the frit for 3 hours at 68 rpm on a ball mill.

4. Remove all material passing the 48 mesh screen. Approximately half of the frit will pass the 48 mesh screen.

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5. Mill the remaining frit at the same speed for approximately 5 more hours or until less than 1/2% of the frit is contained on the 48 mesh screen. Discard the material retained on the 48 mesh screen.

6. Weigh all of the ground frit and return to the ball mill.

7. Add 20 parts of -400 mesh 17-7 PH stainless steel powder per 100 parts of ground ACA 100-1 frit already in the mill.

8. Add 160 parts of water and mill the mixture for 1 hour. Additions up to 240 parts of water may have to be made to make flowable slip. A dip weight test of 35-45 gr/ft^2 should be obtained.

9. Continue wet milling until all but 1/2% cf the material passes the 200 mesh screen. This takes approximately 3 hours.

10. The slip should be discarded after 3 days or at any time there is evidence of crystals forming in the slip.

APPLICATION OF THE ADHESIVE

The ceramic adhesive can be applied to the adherend surface either by dipping part or all of the adherend in the slip or by spraying the slip onto the adherend. If dipping is done, the slip on the back side of the adherend must be wiped or squeegeed off before placing the adherend on the firing tray. Otherwise, an undesired joint may result. If spraying is the application method, care must be taken to spray evenly. Boeing used spraying, dipping, and brushing. Aeronca found that spraying gave superior results in honeycomb panel fabrication. The University of Illinois, in their small-scale specimens, used dipping. Repeated dipping may be required to build up the coating.

After the slip has been applied to the adherend surface, the water must be driven off before the top adherend can be put in place. Although drying can safely be done in a baking oven at a temperature just in excess of the boiling point of water, care should be taken to avoid excessive temperatures or heating rates

during the period of water removal. These can result in shrinkage cracking of the bisque, as the dried green (unfired) ceramic is called.

A fourth possible method of applying the ceramic adhesive consists of pre-forming a bisque sheet in a mold and manually placing it on the adherend. This method is not as satisfactory as the others because of the fragility of the bisque.

Thickness of the adhesive in the finished bond may be controlled by means analogous to the method used with organic adhesives. A spacer layer of metal screen of known thickness can be incorporated into the joint, or shims can be used.

Aeronca's procedure for applying the adhesive, including a prefiring step for easier handling during assembly, is as follows:

Applying Adhesive to the Facing Sheets

A. Heat the skins to be coated to 350 F $\pm$ 20 F. One of several heating methods can be used. Maintain this temperature during the coating operation.

B. Shake the ACA 100-1 slip thoroughly. Do not use slips over 3 days old or slips containing crystals.

C. The spray gun and accessories suggested for this use are:

    1. Binks, Model 18, stainless steel spray gun

    2. Binks, 64PA, stainless steel cap

    3. Binks, 64VT, stainless steel nozzle

    4. Binks, Model 80, pressure cup.

D. Fill pressure cup with ACA 100-1 adhesive.

E. The technique for spraying material can be learned only by experience. The following suggestions may assist in developing the technique:

    1. Slips applied too rapidly will form undesirable glossy bisques.

    2. The best results have been obtained with air pressures between 40-60 psi and pot pressures between 2 and 5 psi.

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3. The rate of spraying of material, the rate of flow of atomizing air, and the proximity of the gun to the sheets are adjusted to control the applied slips. The viscosity of the slip itself will affect all of these adjustments.

F. All spraying is done with the gun normal to the surface.

G. Apply a coat of adhesive by cross coating to result in a 0.006-inch to 0.007-inch dry bisque.

H. Allow 5 minutes for bisque to dry thoroughly.

I. Spray a second coat repeating G and H above.

J. Spray a third coat of the same thickness. The final bisque thickness should be approximately 0.018 inch $\pm$ 0.002 inch. The thickness may be checked by weight. The total dried bisque should weigh 0.35 $\pm$ 0.05 gram/sq.in. Allow adhesive to dry for a minimum of 30 minutes.

K. Prefire by placing the hot coated skins immediately in the furnace at 1750 F for 8 minutes. Skins should be in a horizontal position.

L. Remove from furnace and air cool.

Applying Adhesive to the Core

A. A sample piece of core should be weighed. This sample should be sprayed simultaneously with the core being prepared for use. In some cases, the core itself can be weighed for checking purposes.

B. The core should be sprayed quite wet - almost to the point of flowing.

C. Spray one coat with the core held in such a position that all of cell walls facing the gun are coated. Repeat the procedure, rotating the core 90 degrees after each application, until all the cell walls have been sprayed in a position facing the gun.

D. Invert the core and repeat Step C.

E. Dry the adhesive at room temperature for a minimum of 4 hours.

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F. Dry under heat lamps for a minimum of 30 minutes.

G. Weigh sample piece of core and determine the pickup in grams per square inch of core.

H. If the pickup is insufficient, repeat Steps C through G until the desired pickup is achieved. The travel rate of the gun and the material flow may be varied to add small amounts of adhesive.

I. The desired pickup of bisque for the 0.500 inch, 1/4-inch cell, 0.02-inch foil honeycomb core used in this program is 2.5 to 3.0 grams per square inch of core.

J. Place in the furnace at 1750 F for 4 minutes. Core should be in horizontal position.

K. Remove from furnace and air cool.

ASSEMBLY AND FIRING

After assembly of the joint, it is placed in the furnace under a pressure that has been experimentally determined to be sufficient to result in exudation of molten glassy phase from the joint during firing. Trays, weights, and fixtures of stainless steel, a superalloy, or a suitable ceramic should be used within the furnace. These oxidation-resistant materials are necessary because the firing of ceramic bodies is done in an oxidizing atmosphere to avoid the occurrence of reducing reactions at the surface of the ceramic.

The firing temperature is dictated by the melting range of the ceramic and is limited by the metallurgy of the adherend alloys. In the inorganic adhesive development studies the final adhesive firing was combined with the austenite conditioning or solution treating of the adherends. This required that the ceramics used mature at temperatures between 1750 and 2000 F. From the standpoint of the adhesive, it is desirable that the firing temperature be about 200 to 300 F above the maximum service temperature of the joint.

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TOOLING AND FIXTURING

Tooling and fixturing for bonding with inorganic adhesives is similar to that
used with organic adhesives, with due allowance for the higher temperatures involved.
Since inorganic adhesives have not been used commercially in production of large
parts, elaborate tooling, such as exists for organic-adhesive-bonded aircraft parts,
has not been built. Large autoclaves and electric blankets are clearly impractical
for the temperatures required with inorganic adhesives. Furnaces are usually re-
quired, although quartz heat lamps have been successfully used.

Figure 41 shows a cross section drawing of Aeronca's fixture for making honey-
comb panels. It is analogous to fixtures used in fabricating such panels by organic-
adhesive bonding or by brazing. The tool is essentially a flat stainless steel
trough in which a sandwich to be bonded is enclosed and held under vacuum. The
"Glasrock" base is separated from the panel by an 0.045-inch-thick indexing plate
and an 0.012-inch-thick slip sheet. Edge member bars maintain dimension require-
ments. An additional slip sheet, "Fiberfrax", and an additional indexing plate
complete the layup. An 0.012-inch stainless steel lid is welded to the flange of
the tool. Heat balance is achieved by placing several layers of a "Refrasil"
blanket on the pan assembly.

Assembling the Sandwich

A. Place the "Glasrock" base at the bottom of the trough.

B. Place the edge member bars in place on the "Glasrock" slab and connect with
shear pins.

C. Center one 0.045-inch-thick stainless steel buffer plate on the "Glasrock".
This and the 0.012-inch-thick slip sheet should be evenly coated with a
deposit of levigated alumina.

D. Assemble the sandwich.

E. Place the additional slip sheet on the sandwich, followed by a 0.080-inch-
thick "Fiberfrax" sheet.
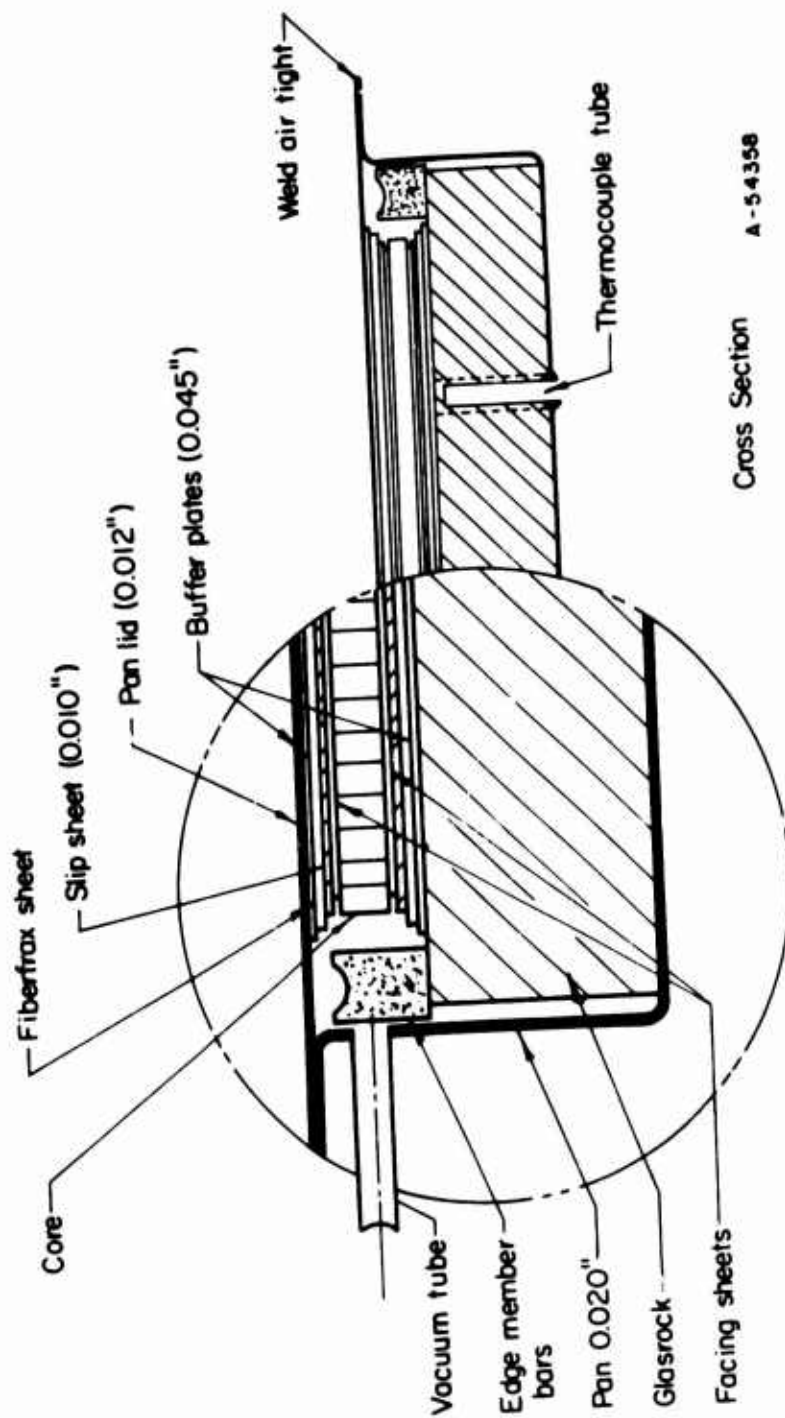
FIGURE 41. TYPICAL CERAMIC ADHESIV BONDING VACUM PRESSURE FIXTURE (Ref. 108)

F. Place the second 0.045-inch-thick buffer plate on the "Fiberfrax" sheet
    to complete the layup.

G. Locate the lid properly and hold in place with weights. Weld the lid
    airtight onto the pan flange.

H. Pull a 5 psi vacuum on the envelope. Any leak detected should be repaired
    before any further processing.

I. Place several thicknesses of "Refrasil" blanket over the pan assembly.

J. Place the tool in the furnace, heat the panel to the proper temperature
    (1700-1750 F) as rapidly as possible, and hold in this temperature range
    for 10 minutes.

K. Remove the tool from the furnace and air cool until the panel temperature
    is 200 F.

L. Remove the panel from the tool, place in a -100 F environment, and hold
    at this temperature for at least 8 hours.

M. Age the panel at 950 F for 60 minutes.

FINISHING THE JOINT

During firing, a scale will be formed on the adherend surfaces. If it is
objectionable, the scale can be removed by one or another of the conventional scale-
removal techniques, such as pickling, sandblasting, vapor honing, or machining.

EXOTHERMIC ADHESIVE BONDING

A novel firing technique for adhesives was developed by the Narmco Research and
Development Division of Whittaker Corp. in which the curing of a ceramic adhesive is
accomplished by heat from an exothermic reaction of the oxidation-reduction type
within the bond line (Ref. 109). As in the case of conventional inorganic adhesive
bonding, presence of a glass phase after exotherm was found to be necessary. The
adhesives also contained a reduced metal phase, either silver or copper, after firing.

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The compositions of the reactant and product mixtures for the adhesives as finally developed are shown in Table V. These systems gave bonds to 17-7 PH stainless steel adherends with lap-shear strengths in excess of 9000 psi at all temperatures up to 800 F. Exothermally brazed PH 15-7 Mo stainless steel honeycomb panels were compared with furnace brazed panels, with the following results:

	Exothermally Adhesive Bonded Panel	Furnace Brazed Panel
Flexure Strength, psi	84,300	160,000
Edgewise Compression Strength, psi	61,900	115,000

Although the exothermic reactions were started by heating the entire joint in a furnace during the development program, an igniter is visualized as an initiation source in practice. The promise of the method lies in the possibility of making bonds under conditions where power sources or heavy equipment are not available, such as in space. So far, only bonds of a few square inches in area have been made. Considering the limited amount of development work, the results are encouraging, but considerable additional development would be required for a practical system.

TABLE V. EXOTHERMIC SYSTEMS (Ref. 109)

System	Overlap Bonding Adhesive Compositions, wt percent	Heat cal/gm
NX-S1 Silver Base	9.4% Mg + 2.9% B + 36.6% Ag_2O + 32.2% CuO + 2.0% Ag + 7.6% SiO_2 + 3.3% Borax $(Na_2O.2B_2O_3)$ + 6.0% halides* + air = 34.8% Ag + 24.4% Cu + 15.2% MgO + 7.5% SiO_2 + 1.0% Na_2O + 11.3% B_2O_3 + 5.8% halides	486
NX-C1 Copper Base	7.2% Mg + 34.7% Cu_2O + 4.1% SnO_2 + 4.6% $(Na_2O.2B_2O_3)$ + 10.5% SiO_2 + 4.1% B + 26.8% CuO + 2.0% Cu + 6.0% halides* + air = 52.2% Cu + 3.0% Sn + 11.6% MgO + 10.2% SiO_2 + 15.9% B_2O_3 + 1.3% Na_2O + 5.8% halides + 3.0% Sn	503

Honeycomb Bonding Adhesive

System	Overlap Bonding Adhesive Compositions, wt percent	Heat cal/gm
NX-S2 Silver Base	7.7% Mg + 3.4% B + 30.2% Ag_2O + 37.1% CuO + 2.3% Ag + 8.7% SiO_2 + 3.7% $(Na_2O.2B_2O_3)$ + 6.9% halide* + air = 29.6% Ag + 28.8% Cu + 12.4% MgO + 13.0% B_2O_3 + 8.4% SiO_2 + 1.1% Na_2O + 6.7% halides	473

* Halide composition: 3.3% KHF_2 + 2.0% Li_2F + 0.6% KCl + 0.1% Pluronic L-61.

APPLICATIONS

There are relatively few production aerospace applications of adhesive bonding
of stainless steels. By comparison, welding and mechanical fastening applications
are much more frequent. Where adhesive bonding has been used, however, performance
of the joints has been from satisfactory to excellent. Adhesive bonding is a possi-
ble joining method for stainless steels that should be considered by designers for
applications within the capabilities of the newer adhesive systems.

AFT-END CLOSURE FOR POLARIS A-3 MOTOR CASE

Although it is not a production application, the experimental use of 0.005-
inch-thick Type 304 stainless steel reinforcement patches on the Polaris A-3 aft-
end closure is included because it is representative of a class of secondary joints
(Ref. 110). The adhesive used to bond the stainless steel to the subscale filament-
wound dome was a modified epoxy. The patches were placed between plies of the dome.
The completed dome was pressure tested and failed by one patch tearing along a
shear line in the structure. Adhesion of the patches to the glass fiber-epoxy
structure was reported as being generally excellent. A schematic drawing of the
dome configuration, showing locations of the stainless steel patches, is shown in
Figure 42.

HELICOPTER ROTOR BLADING

Rotor blades for helicopters are commonly fabricated using adhesive bonding as
the joining technique. Rotor blades are being produced in large numbers at the
present time. They consistute the most important example of adhesive-bonded primary
structure involving stainless steel in the aerospace field. Adhesive bonding is
the preferred joining method in the rotor blade application because of good fatigue
strength, possibility of producing smooth, accurate airfoil blade shapes, and ability
to join dissimilar metals.

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Patches overlapped 1.0 inch

Tangent line

A-54359
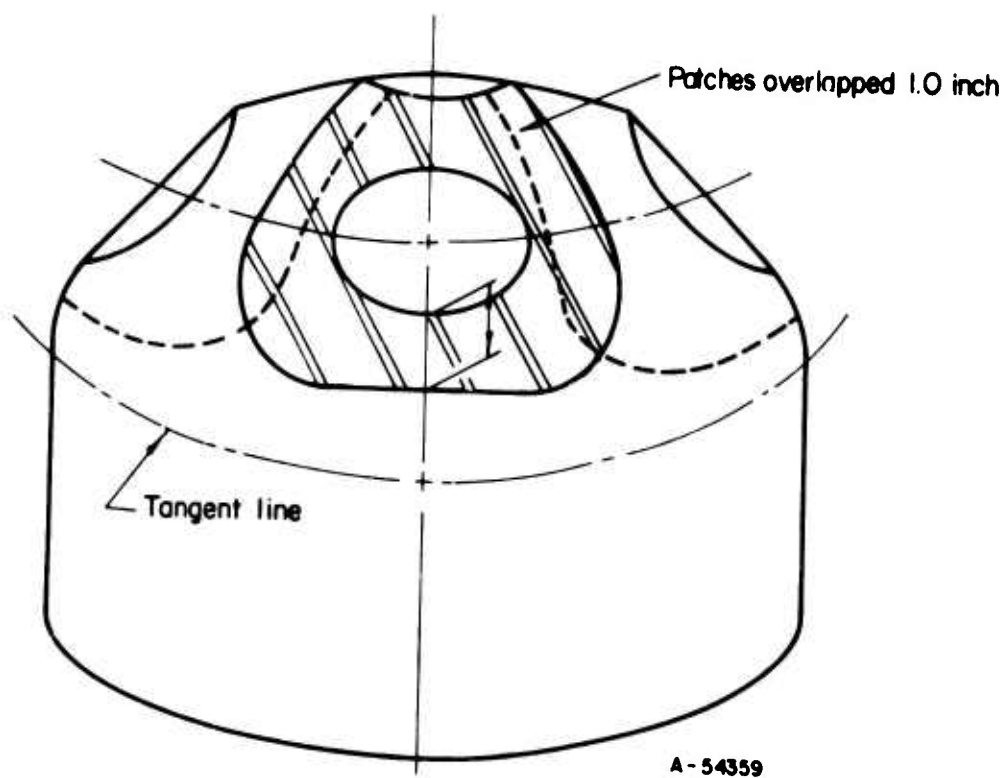
FIGURE 42. LOCATIONS OF ADHESIVE-BONDED REINFORCEMENT PATCHES ON
AFT-END DOME OF POLARIS A-3 MOTOR CASE. (Ref. 110)

Stainless steel appears in present rotor blades as the leading edge erosion shield. Bell helicopter uses stretch-formed Type 301 or 302 stainless for the erosion shield on all but the outer three or four feet of the blade. Hastelloy X, a stronger cobalt-base alloy, is used near the blade tip, where linear velocities are highest (Ref. 53). The stainless steel leading edge is bonded to a brass substrate that serves as a ballasting weight as well as a solid backup for the stainless steel. On present blades, the remaining portion of the cross section, from about the maximum chord to the trailing edge, is made of aluminum. On smaller blades, the airfoil shape of the aluminum skins is maintained by extruded aluminum internal stiffener sections. On larger blades, tapered aluminum honeycomb is used. Stainless steel doublers and pressure pads are also bonded to the blade in the vicinity of the hub. All of the adhesive-bonded joints are autoclave cured simultaneously. Blades under development for helicopters of advanced design will incorporate a greater proportion of stainless steel parts, both conventional and precipitation-hardening.

HELICOPTER FIREWALL

A stainless steel face sheet is used in present helicopter firewall panel construction (Ref. 53). The stainless steel sheet, singly curved, is bonded to an aluminum honeycomb core. A glass-reinforced phenolic face sheet is used on the opposite side of the core.

CONCLUSIONS AND RECOMMENDATIONS

Work is already under way on most problems associated with adhesive bonding of
stainless steel. Actually, these problems are the same as those encountered in
adhesive bonding in general and fall into four categories. These are: adhesion,
adhesives development, processing, and service behavior. The problems in each of
these areas are discussed separately below.

ADHESION

Despite years of research concerning forces of adhesion, man is still unable
to predict in any detail its occurrence or nonoccurrence. If calculations based
on our present knowledge of molecular forces were accurate, we would probably be
in trouble of another kind, with things sticking together because, according to
these calculations, adhesion should occur much more generally and between a far
wider range of materials than it does. That it does not, indicates our knowledge
is incomplete. There are two major areas regarding adhesion in which greater
understanding is needed. The first is the role of surfaces in adhesion; the second,
closely related, is the role of surface film.

Study of surfaces is difficult because of the problem of distinguishing pro-
perties of the two-dimensional surfaces from those of the underlying solid or
liquid. However, techniques such as ion-emission microscopy and low-energy elec-
tron diffraction are being used to study surface phenomena. Such studies should
yield useful information regarding adhesion and are recommended.

In the area of surface films, it is known that oxide films and layers of
absorbed gases often prevent adhesion. It is also known that naturally occurring
films will always be present in normal atmospheres and that other films are often
deliberately added to surfaces. (These are added for either corrosion resistance
or a more attractive surface.) What is not understood in any detail is what are
desirable properties of surface film for maximum adhesive qualities. The authors
know of no work being conducted to gain such understanding.

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Such work is necessary, however. As stated in this report, reaction products, in the form of films, are created in the surface preparation of stainless steels for adhesive bonding. The composition of these surface films will only be indirectly related to the adherent alloy. It would appear safe to assume that an adhesive molecule would bond to this surface film, and be unaware of the nature of the metallic adherend. Because of the lack of understanding of these films, surface treatment for adherends is often an arbitrary thing. Thus, greater understanding of these films is imperative. Again, investigation is difficult because distinctions must be drawn between the bulk and surface effects of both the film and actual surface. It is recommended that studies be undertaken to gain an understanding of effects of film on adhesion through the study of extremely thin vacuum-deposited and electroplated films for electronic application.

ADHESIVES DEVELOPMENT

Unlike the area of adhesion, there is a great deal of activity in the development of adhesives through tailoring of molecules for particular applications. Much work is being done to develop heterocyclic adhesives. These promise to answer the urgent need for organic adhesives for use at higher temperatures. They also appear to be good room-temperature adhesives and to have superior radiation resistance as compared to other organic adhesives. On the other end of the scale, polyurethanes appear to be satisfactory for use at liquid-hydrogen temperatures. Their temperature strength dependence down to -423 F would indicate that they will perform at even lower temperatures, perhaps at liquid-helium level and on to absolute zero. This has yet to be demonstrated, however. Studies should be started which will determine their usefulness at these extremely low temperatures.

There are several problems yet unanswered in the development of inorganic adhesives. Application of inorganic adhesives would be in high temperature structures. The problems to be solved involve ductility, bond strength, and maturing temperatures.

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PROCESSING

In developing adhesives, care must be taken to keep them practical from the manufacturing viewpoint. A good adhesive should be easily applied, non-toxic, inexpensive, tolerant of shortcomings in adherend preparation, and it should cure at room temperature, or with only a short, moderate-temperature curing cycle. It will, of course, not always be possible to produce a high-performance adhesive with all these qualities, but they should always be kept in mind.

There are several examples of recently produced adhesives that use new methods of handling, applying, and curing, but more work is needed in the area. Among those produced are internally heated film adhesives and room temperature curing epoxy film. Another example is chemically blocked adhesives, such as silicone sealants. A particular need, as yet unperfected, is for mechanically blocked adhesives. In these, hardeners, encapsulated in frangible membranes throughout the resin, are activated by mechanical rupture of the membranes. Needed to accomplish this are membrane materials that will withstand chemical action of resin and hardeners. The entire area of mechanically blocked adhesives development is in need of continued research.

SERVICE BEHAVIOR

Further work is needed in the testing of bond strength and of useful life of adhesive-bonded joints. There are presently nondestructive techniques for testing as-welded bond strength. However, they should be further refined to allow detection of in-service or postexposure loss of bond strength.

Environmental factors effecting useful life of adhesive bonds are temperature, humidity, stress, and time. Procedures are needed to test the combined interaction effects of these factors.

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ADHESIVE BONDING OF STAINLESS STEELS

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The information in this report has been reviewed for security classi-
fication. Review of any information concerning Department of Defense or
Atomic Energy Commission programs has been made by the MSFC Security
Classification Officer. This report, in its entirety, has been determined
to be unclassified.

This report has also been reviewed and approved for technical accuracy.

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